SURFACE OPTIMIZATION OF SILOXANE-POLYURETHANE MARINE COATINGS FOR IMPROVED FOULING-RELEASE PROPERTIES

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DOCTOR OF PHILOSOPHY

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ABSTRACT

Biofouling has been an economically and environmentally costly problem to mankind ever since they set sail. Biofouling causes frictional drag leading to slow vessel speeds, and increased fuel costs. Antifouling (AF) coatings containing biocides have been used for decades, however, since some biocides have shown undesired effects towards the environment, a non-toxic solution to combat fouling is desired. Subsequently, fouling release (FR) coatings quickly gained acceptance as a non-toxic approach to contend with biofouling. Unlike AF coatings, FR coatings not necessarily prevent settlement of organisms, they permit weak adhesion which is easily released by water shear or light grooming.

The siloxane-polyurethane (SiPU) coatings based on the concept of self-stratification is a non-toxic and durable approach to prepare FR coatings. In this work, several approaches were considered to optimize surface properties of SiPU coatings. Incorporation of phenyl-methyl silicone oils led to improved FR properties towards several marine organisms in laboratory assays and in ocean field immersion. Enhancement in FR properties may be attributed to slowly exuding silicone oil providing surface lubricity, weakening the adhesion of marine organisms.

Addition of diphenyldimethyl siloxane in to SiPU coatings at different ratios resulted in micro-scale surface topographical features which negatively affected microfouling-release while several coatings displayed good FR performance towards macrofouling organisms. In another study, decreasing the acid group content helped to improve FR performance towards barnacles, but FR performance towards diatoms were compromised.

Novel amphiphilic siloxane-polyurethane (AmSiPU) coatings from polyisocyanate pre-polymers modified with polydimethyl siloxane and polyethylene glycol displayed excellent FR properties towards several marine organisms during laboratory assays. These AmSiPU coatings show promise as contenders to commercial FR standards. Initial development of SiPU coatings with hydrophilic surfaces showed promise, as the coatings showed rapidly rearranging surfaces with comparable FR performance to commercial standards which claim hydrophilic surface properties.

During freshwater field immersion trials, SiPU coatings displayed excellent mussel FR performance up to 3 years. Surface analysis suggested that solvent content affected self-stratification and morphology of SiPU coatings. The SiPU coating system is a highly tunable, tough, environmentally friendly, and practical FR solution which can evolve along with non-toxic commercial marine coatings.

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DEDICATION

I dedicate my dissertation to my mother Sujeewa Dharmasena, and my father Galhenage Rupadeva for their sacrifices, providing everything I needed to pursue my education (even if it was thousands of miles away from home), and encouraging me to do my best. I would not be able to achieve this goal without your support.

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CHAPTER 1. GENERAL INTRODUCTION

Marine Biofouling and Impact

Marine biofouling is defined as the settlement and growth of marine organisms on all surfaces that are immersed in seawater.[1] Marine biofouling is a global concern affecting the shipping/ maritime industry with both economic and environmental consequences.[2] Accumulation of fouling on ship hulls cause increased roughness contributing to frictional drag leading to severe loss in fuel efficacy.[1, 3] Increased fuel cost due to frictional resistance can be an additional 40% which may contribute to a 77% increase in overall voyage cost.[1] On the other hand, heavy fouling of the ship hull requires frequent visits to the dry-dock, costing the ship owner time, resources, toxic-waste and ultimately money.[1] Marine biofouling also has detrimental effects on protective paint of the ship hull.[1] Chemical nature of the adhesives and waste products from the organisms may contribute to the deterioration of marine coatings making the ship hull susceptible to corrosion and degradation. Transport and release of non-native organisms into far-away oceans poses a huge environmental threat with regard to transport of invasive species, causing concerns for imbalanced marine ecosystem.[1, 4] Given the widespread network of global shipping routes, the risk of spreading invasive species (hull-mediated species transfer) can be very high.[5] Marine biofouling can also indirectly contribute to another environmental concern; greenhouse gas emissions.[2] Significant increase in fuel consumption may lead to increased emission of greenhouse gases releasing air pollutants.

Marine biofouling is a complex process that involves more than 4000 marine organisms.[1, 3] If the surface remains the same, several factors of the surrounding marine environment can affect the extent of fouling, type and settlement of marine organisms, diversity of biofouling communities and their adhesion strength. These factors include salinity, nutrients, temperature of water, flow of currents, sunlight, ions and minerals present in the surrounding marine environment.[6, 7] Marine organisms have shown diverse adhesion mechanisms making it difficult for a specific coating to prevent their adhesion.[8] On the other hand, the miracle of nature has allowed these organisms the ability to recognize and respond to surface cues allowing them to show adaptive behavior.[2, 9, 10] Therefore developing a marine coating system to combat biofouling is not an easy task. A potential coating solution for marine biofouling must constitute economically feasible, environmentally friendly (non-toxic), durable, easy to use system with effective performance towards all zones of oceans and all types of marine organisms.

Biofouling Process

Although most literature presents a simple successive model for biofouling,[1, 11, 12] recent studies and understanding of the biofouling process presents a more complex dynamic model with considerable interactions and interplay of marine organisms.[2, 3, 7] When a fresh surface is exposed to the marine environment, a conditioning film is formed due to absorption of organic molecules. Once the surface is conditioned, it is ready for wide range of marine organisms to explore, settle and to form communities. Due to the dynamic nature of biofouling, attachment of marine organisms can be a combined effect of surface chemistry of the substrate, nutrients available, competition and predation.[13, 14] In a time scale of seconds, marine bacteria, diatoms, and protozoa contribute to micro-fouling forming biofilms (slime) on conditioned surfaces.[2, 3] Within a few minutes to hours, soft fouling algae spores, tunicates, and sponges also adhere to surfaces along with larvae of barnacles, mussels, hydroids, and tubeworms contributing to macro-fouling.[2, 3] Studies have reported that different species of the same organism can be found to colonize separate locations of the ship hull.[10, 13, 15] Hence biofouling is much more complex phenomenon and a systematic understanding of biological processes involved during organism settlement, adhesion and colonization is essential to find practical solutions.

Economic Impact

The magnitude of economic impact from biofouling is astounding. Although biofouling has a major economic impact on the oceanic transportation sector, it can also have a significant effect on modern day energy production (off shore oil rigs, hydropower turbines, wind mills and wave power generators). However in this section, the economic impacts due to hull fouling is discussed. The effects of fouling on frictional drag have been long studied and reviewed (1952).[16] The results clearly indicate that fouling on ship hulls leads to a considerable increase in frictional drag. However the magnitude of increase depend mostly on the fouling type and extent of coverage.[16-19] Schultz *et al.* described a method to predict the ship's resistance and powering due to drag based on laboratory-scale drag measurements and boundary layer similarity law analysis.[16] He later used this method to estimate economic impact due to biofouling on a range of vessels and the predictions are consistent with results from ship powering trials.[16, 19] These studies highlight that the cost for increased fuel consumption is far more greater than the cost for painting, dry-docking and hull cleaning.[19] Estimates from the United States Navy Naval Sea Systems Command indicate a 6-45% (depending on the size of vessels) increase in fuel cost alone due to 2% loss of operating speed.[12] Schultz *et al.* predicted that additional powering costs due to slime (light fouling) can be 10-16% increase while that for heavy calcareous fouling may add up to 86%.[16] A study conducted to estimate the economic impact of fouling on mid-sized naval surface ships (Arleigh Burke DDG-51, 30% of the entire navy fleet) in The United States Navy, found that hull fouling for the DDG-51s cost US$56 million per year.[19] If they were to extend their predictions to the entire fleet of United States Navy ships, the hull fouling cost can be US$180-260 million per year.[19] However considering the direct and indirect sources, cost of biofouling for the United States Navy may tower up to approximately US$1 billion per year.[10]

Strategies for Combating Biofouling

In the early days of shipping, ship hulls are typically made of wood and a variety of strategies were explored for preventing biofouling. Wooden ship hulls were protected with copper, lead, tar, wax, asphalt and other materials available depending on the region.[1, 3, 20] Soon after iron was used for building ships, copper and lead sheathing were widely used for combating biofouling.[20] Since this strategy accelerated deterioration due to corrosion, anti-fouling (AF) paints with toxins emerged as a potential solution.[20] These early stage AF paints were prepared by dispersing toxins in to natural binders (linseed oil, tar and rosin) which set the standard for AF paint systems. The toxins used in AF compositions were later known as biocides.

Starting from the 1900s, effective AF compositions with active biocides were widely explored.[1] Eventually organotin compounds were identified as very effective AF ingredient and in the 1960-1970s AF coating compositions composed of self-polishing copolymers and tributyl-tin (TBT) were introduced.[1, 3, 20] The release of TBT was controlled via the hydrolysis of organotin-ester linkage. The active ingredient TBT was slowly released as the polymer eroded. These AF paints with TBT were very effective against biofouling; TBT was toxic to targeted marine organism essentially killing them as they came into contact with the ship hull.

Although TBT based AF paints were highly successful in preventing marine biofouling, leaching of TBT posed a great threat to non-targeted marine organisms. First reports of oyster shell thickening were reported from France.[21] TBT led to the extinction of some marine organism such as Nucella due to its interference with their reproduction process.[22] A few decades later, accumulation of tin in fish, seals and ducks was also observed.[3] Therefore the success of TBT based AF coatings were short lived and copper oxide based AF coating gained significant attention. The international Maritime Organization started restricting the use of TBT from the early 2000s. Use of TBT in AF compositions was completely banned in 2003 and TBT based AF paints were required to be removed from vessels by 2008.[3]

Today, AF coatings with copper oxide or organic biocide contribute to majority of marine coatings in the market.[21] Although not as severe as TBT based paints, AF coating systems with biocides also have negative environmental effects on marine life and they are less sustainable.[3, 7] Release of copper oxide has led to accumulation of copper in ports due to extended docking periods. Release of organic biocides also poses a threat to local ecosystems. On the other hand, extensive amount of laboratory toxicity data and risk assessments are required for new biocides to emerge and to be used in AF paints.[3, 23] Few number of organic biocides (12-15) remain on the approved list to be used as an ingredient in AF coating compositions.[3] Given all the negative impacts of AF coatings and the continued push by environmental agencies, non-toxic alternatives are being widely explored.[7]

Non-toxic Marine Coatings

In the effort to find non-toxic solutions to combat biofouling, coatings with the ability to release fouling due to hydrodynamic force became an area of research and technical interest. Although fouling-release (FR) coatings were introduced in 1961 as a non-toxic alternative to AF coatings, their existence was over shadowed by the excellent performance of the TBT-based self-polishing AF paints. Fouling-release coatings started to gain market acceptance in 1990 to 2000 when the use of TBT in AF paints was heavily regulated and leading to complete ban of TBT in 2003.[1, 3] Fouling-release coatings do not include any toxic AF ingredients to inhibit fouling, rather they have a surface that allows marine organism to adhere weakly.[1, 3, 12] Ideally, fouling would be washed off by hydrodynamic force (self-cleaned) or fall off due to the weight of organisms (macrofouling organisms like barnacles can grow to have a height of 3-5 cm).

Typical FR coatings are designed to minimize the adhesion strength of marine organisms by using a low surface energy and low modulus material for top-coating surface. Low surface energy materials minimize wettability of some adhesives secreted by marine organisms leading to weak interfacial bond/ adhesion allowing release with low force.[2] On the other hand having low modulus affects the release of organisms by allowing easy peel off from the coating surface. Robert E. Baier experimentally determined the effect of material surface tension on bio-adhesion. He found that the critical surface tension of materials for minimum bio-adhesion was around 22 mN/m (Baier curve).[24] Further a fouling release zone (20-30 mNm^{-1}) based on surface tension materials was recomended.[24] Fracture mechanics show the relationship in regard to removal of a stud from a rigid surface. In the case for adhesion of marine organisms the surface can be considered as the protective coating and the stud as the organism (Figure 1.1). Considering fracture mechanics equation (Eq 1.1) low elastic modulus results in smaller critical force for removal.[3] Therefore removal or release of adhered organism is a combined effect of surface tension (related to work of adhesion w_a) and modulus of the coating material.

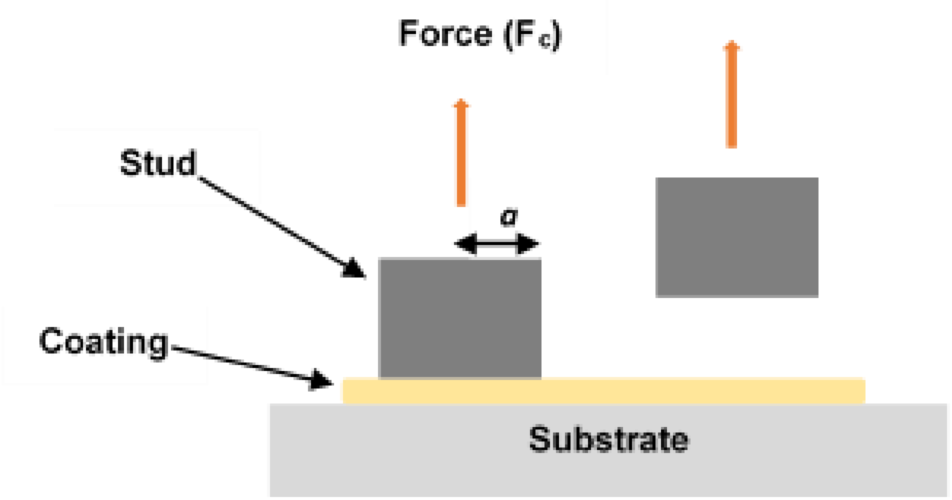

Figure 1.1. Schematic representing release of a stud glued to an elastomeric coating on a rigid substrate

$$F_c = \pi a^2 \left[\frac{8Ew_a}{\pi a(1-\nu^2)}\right]^{1/2} \qquad \textbf{(Equation 1.1)}$$

Where F_c is the critical push off force, a is the radius of the stud, E is the elastic modulus of the material the stud is adhered to, w_a is the work of adhesion between the stud and the coating, and ν is the Poisson's ratio for the coating material.

Polydimethyl siloxane has a surface tension of ≈22 mN/m and an elastic modulus of 0.5-5 MPa. Polydimethyl siloxane (PDMS) elastomers satisfy both surface tension and modulus requirements for minimizing bioadhesion. Therefore, PDMS elastomer based materials are commonly used in most FR coatings.[1, 25] However, PDMS elastomeric coatings have poor mechanical durability (soft and rubbery) leading to easy surface damage.[6, 26] Due to the low surface energy, obtaining sufficient adhesion to underlying paint layers (primer) is extremely difficult. A tie coat is commonly used to enhance adhesion of FR top coat to subsequent paint layers. However the adhesion of top coat on to subsequent paint layers is still a problem.[6, 26] On the other hand PDMS is a relatively expensive polymer compared to typical polymers used for coatings. However PDMS combine some unique features which is often difficult to achieve with other organic polymers. They are chemically and thermally stable, non-toxic to marine organism, and use well known chemistries for crosslinking.[27] PDMS based polymer chains are very flexible which arise from the silicon oxygen bond in the backbone. The silicon oxygen bond has wide bond angles which allows easy rotation around the polymer backbone to configure into thermodynamically stable state. This flexible nature of PDMS contributes to the surface rearrangement to provide low surface energy surface. For these reasons PDMS elastomers make good FR coating systems with tunable properties.

Siloxane-Polyurethane (SiPU) Fouling Release Coatings

Existing commercial FR coating systems are still based on soft silicone elastomers. Although they perform fairly well, concerns related to coating durability and adhesion still need to be addressed. The siloxane-polyurethane (SiPU) hybrid coating system developed at NDSU, targeting FR applications, was designed to overcome the shortcomings of PDMS elastomer based FR coating systems.[28, 29] Crosslinkable SiPU composition was developed by combining a reactive siloxane resin with polyurethane in a single coating system. When applied, the siloxane self-stratifies to the surface and the polyurethane comprises the bulk material. Self-stratified siloxane layer on the surface provides FR properties while the polyurethane provides toughness and adhesion to primer. Due to the crosslinked nature of the coating, the siloxane layer (top surface) and the polyurethane layer (bulk) are locked in place providing excellent long term stability during exposure to water.[30, 31] Figure 1.2 shows a representative image of the SiPU coating system.

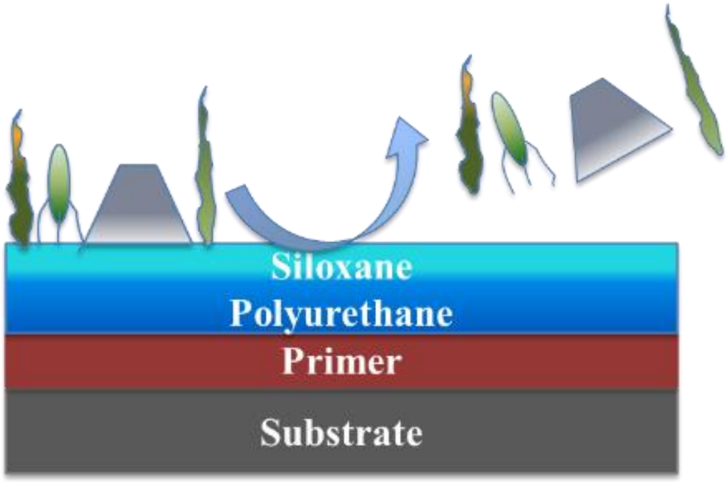

Figure 1.2. Self-stratified, crosslinked siloxane-polyurethane (SiPU) coating system. The top layer is concentrated with siloxane providing FR properties and polyurethane bulk adhering to primer surface

The typical SiPU coating system consists of amine terminated siloxane resin, an acrylic polyol, polyisocyanate, catalyst and pot-life extender. The SiPU coating system composition was optimized using combinatorial and high throughput experimentation in terms of formulation ingredients and several studies have demonstrated the fouling release performance.[31-37] Siloxane-polyurethane coatings demonstrated comparable FR properties to commercial standards during laboratory biological assays (for bacteria, algae, and barnacles) and field immersion trials.[35, 37-39] Given the durability of the SiPU system, it serves as a viable candidate for marine coating applications that can be groomed periodically using an automated device to minimize fouling.[39] The SiPU coating system provides a platform to develop non-toxic durable FR coatings. The versatility of the SiPU system allows easy tuning of FR and surface properties of coatings by modification to one or more ingredients. Previous studies bear evidence to the high level of tunability of SiPU coatings to improve the FR properties.[35-38, 40] Modifications to further improve FR performance of SiPU coatings can be drawn from recently popular strategies for non-toxic marine coatings.

Modern Approaches for Non-toxic Marine Coatings

Developing a non-toxic marine coating system is not an easy task. During the past several years researchers have been exploring multiple strategies to contend with biofouling. However these new strategies need to demonstrate feasibility as a practical solution, cost effective, long performing, environmentally friendly, and highly tunable. Approaches such as bio-inspired surfaces, amphiphilic coatings and hydrophilic/ zwitterionic surfaces appear to be among the most popular topics in the area of non-toxic marine coating solutions for combating biofouling.

Bio-inspired Engineered Surfaces

Nature uses multiple defense techniques to combat fouling.[41] In the search for non-toxic solutions for biofouling, utilizing inspiration from nature or mimicking natural AF/FR mechanisms to engineer surfaces that can defend against fouling is one approach which has gained popularity during the recent years.[12] Marine organisms and plants in aquatic environments have a variety of natural mechanisms to combat biofouling. Some of the natural defense mechanisms include structurally hierarchical topographies, secretion of oils and mucus, replenishing surfaces by sloughing skin layers, release of bio-active molecules and enzymes.[2] In most cases marine organism tend to use a combination of chemical, physical, mechanical and behavioral strategies to combat fouling.[42] These bio-inspired techniques have been closely observed, and attempts have been made to mimic (biomimetic) these mechanisms using modern day materials and to use inspiration from nature to develop novel material solutions to biofouling prevention.[12, 42]

In the area of bio-inspired coatings, much of the research effort is devoted to designing surfaces with topographies that reduce the settlement or promote the easy release of marine organisms. The Lotus leaf effect, texture of marine mammal skin, and other hierarchically complex plant/animal microstructures are a few key concepts that have been investigated for AF/FR coatings.[43-49] Engineered surfaces with topographies inspired by fast moving shark skin were developed in the early 2000s and known as Sharklet™ AF.[44, 50] These Sharklet™ AF surfaces were prepared using PDMS and their effect on biofouling was evaluated varying the size and the scale of the features.[9, 44, 50-52] Interestingly, marine organisms showed a response to surface features although correlating their response to size and scale of textures became a complex undertaking. *Ulva linza* is one of the most common green algae in the marine environment that contribute to fouling on ship hulls. Extensively studied settlement and adhesion behavior of *U.linza* enable it as a tractable model system for evaluating FR coatings.[9, 53-57] SharkletTM AF surfaces with 2µm wide ridges (n3-n5 Figure 1.3) displayed up to 85% reduction in *U.linza* spore settlement.[44, 52] Schumacher *et al.* studied the correlation of spore settlement and engineered roughness index (ERI_1) and found an indirect correlation based on feature size, geometry and roughness of Sharklet™ AF surfaces.[52]

Engineered roughness index (ERI_1) is dimensionless and the ratio is based on Wenzel's roughness factor, depressed surface fraction, and the degree of freedom of spore movement.[52] Highest reduction in spores of *Ulva* settlement for Sharklet^{TM} AF was obtained with the ERI_1 of 9.5 (77% reduction in settlement). Later Magin *et al.* developed the ERI_2 (revised model) which included the Reynolds number and provided a better correlation with observed spore settlement trends with changes in surface topographies. During this study the Sharklet^{TM} AF coating demonstrated significantly less settlement of macroalge *U.linza* and bacterium *Cobetia marina* compared to PDMS coatings with other textured patterns (triangles, ridges and pillars) as well as smooth PDMS coating.[51] Although the suggested model is a useful tool to predict the size and the scale of feature that effectively prevent fouling by one kind of organism, many other organisms (more than 4000) respond to wide variety of length scales. In a recent study Schumacher *et al.* fabricated a structurally hierarchical, complex Sharklet^{TM} AF surface by superimposing two patterns.[58] In laboratory studies, this new Sharklet^{TM} AF showed AF properties towards both *U.linza* and barnacle cyprids.[58] However combination of surface topography features, surface chemistry and modulus in fabricating Sharklet^{TM} AF may provide an effective AF/FR system.

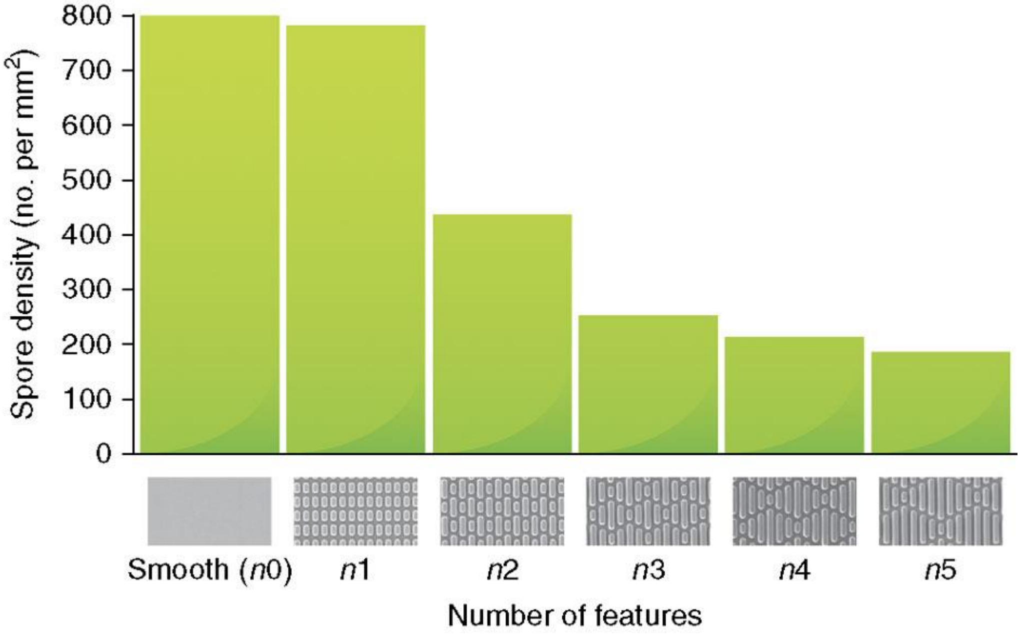

Figure 1.3. *Ulva linza* spore settlement on bio-inspired engineered Sharklet^{TM} AF patterns imprinted on PDMS elastomers. Reproduced from reference [2]

Inspired by the skin of pilot whales (*Globicephala melas, Delphinidae*), micro/nanostructured coatings with fouling resistant/release properties were prepared through layer by layer self-assembly of polyelectrolytes.[49] Figure 1.4 shows a side-by-side comparison of the surface morphology observed for pilot whale (*G. melas*) skin and the bio-inspired surface obtained from polyelectrolyte self-assembly. Coating surfaces with various length scale features were obtained by changing the pH during the spraying of oppositely charged polyelectrolytes (poly(acrylic acid) and poly(ethylenimine)). Other than the effect of the pure morphology, the effect of surface chemistry was also investigated by preparing a second set of textured coatings functionalized with poly(ethylene glycol) (PEG) and tridecafluoroctyltriethoxysilane (TDFTES). The chemical modifications were confirmed by contact angle, X-ray Photoelectron techniques relative to the unmodified coatings. The surface features did show an effect on the settlement of *U.linza* spores; where the lowest settlement was observed for coatings with 2 µm size features which were similar in size to those observed on pilot whales (*G.melas*).[49] Interestingly spores of *Ulva* had a similar response as they did to changes in morphology irrespective of surface chemistry, although the total spore density settled on the coatings showed slight alteration.[49] Higher spore density was observed for coatings modified with TDFTES compared to both PEG modified and unmodified coatings. The study suggested that the observed fouling resistance and release properties of the nano/micro textured coatings were related to capillary forces exerted by the structure which relate to size, roughness and the special arrangement of the microstructure.

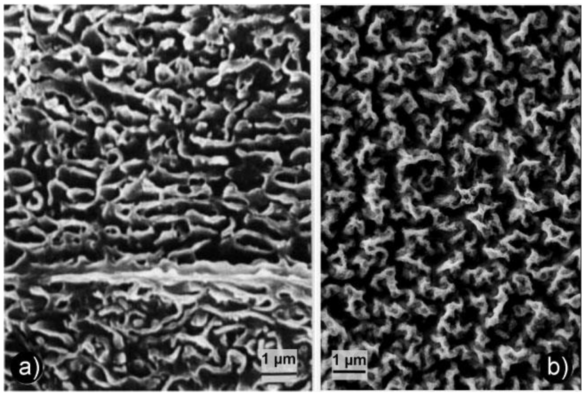

Figure 1.4. Side-by-side view of surface topography features observed on a) skin of pilot whale (*G. melas*) and b) bio-inspired surfaces fabricated by polyelectrolyte self-assembly. Reproduced from reference [49]

In another study, the settlement behavior of zoospores of *U.linza* on “Honeycomb” textured poly(methylmethacrylate) (PMMA) surfaces was observed.[48] A surface with a gradient in feature size varying from 1- 10µm was fabricated by hot embossing a honeycomb structure onto PMMA and the settlement of green algae spores was studied. High settlement of *U.linza* spores was observed for feature sizes greater than the average size of the spores (>2.6 µm). A significant decrease in spore settlement was observed when the size of the features was smaller (1-2 µm).[48] Microscopy images showed that spores of *Ulva* perfectly fit into features with a pit size of 2.6 µm.[48] Thus it was evident that the size of the surface features really matters when spores choose a place to settle or adhere onto. Surface features with sizes smaller than the organism are often observed to be unfavorable for settlement, while features bigger than the organism often enhance the settlement.[9]

Anti-fouling actions of living marine life has inspired some strategies for combating biofouling. Living plants and organisms use physical, chemical, mechanical or behavioral methods to contend with biofouling. Some use the defense mechanisms of releasing toxic or non-toxic chemicals mediated by enzymatic action to deter fouling. Inspired by this aspect of nature, recent studies have demonstrated that an enzyme mediated AF strategy can be incorporated in to coatings.[20, 59, 60] Although not all enzyme mediated AF strategies are considered non-toxic, enzyme based mechanisms that degrade the adhesive, limiting the initial settlement of organisms, may be considered as non-toxic solutions.[60] However enzyme based coatings are very sensitive to temperature, pH, salinity, depletion of activating substrate and flow of hydrodynamic force leading to the rapid loss of AF properties.[20] In a recent study that discussed the use of an enzyme to generate hydrogen peroxide (H_2O_2 environmentally friendly anti-fouling specie) showed quick depletion of AF performance during field immersion in the Indian Ocean compared to the Atlantic Ocean.[59] Significant high temperatures experienced in the Indian Ocean have accelerated the H_2O_2 production leading to fast deterioration of AF properties. Despite their limited success, combining non-toxic enzyme mediated AF with other FR strategies may be a more effective solution to biofouling prevention.

Constant motion or movement of thin hair like cilia is utilized by some marine organisms (mollusks and coral) to prevent the attachment of fouling.[61] A recent study have adapted this inspiration from nature to find a solution for biofouling prevention.[47] The study described a theoretical model and computational simulations investigating the ability of actuated artificial cilia to repel adhesive particles due to an oscillating shear force (Figure 1.5).[47] Modeling the oscillating motion of the artificial cilia in a flow channel allowed for a demonstration that the flow-driven motion of cilia was able to repel adhesive particles. In the marine environment the movement of cilia can be induced by hydrodynamic flow. Findings from this study may lead to bio-inspired, self-cleaning surfaces that repel micro-debris and micro-biological organisms.

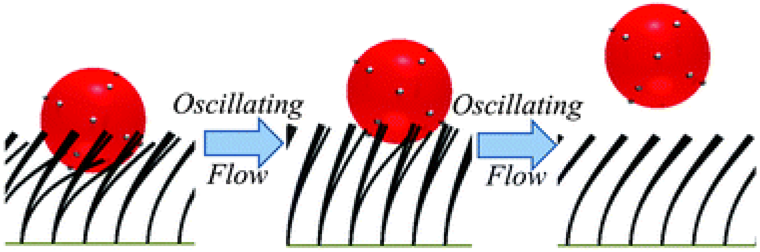

Figure 1.5. Activated, artificial cilia repelling small adhesive particles similar to the process of live cilia preventing biofouling. Reproduced from reference [47]

Slippery liquid infused porous surface (SLIPS) inspired by the slippery surface of pitcher plants has shown success as a non-toxic fouling resistant and release surface.[62] SLIPS are fabricated by infusing a liquid in to a porous mesh with similar surface energy allowing the formation of a highly smooth, dynamic, and liquid-like surface.[45] The infused liquid is immiscible with a variety of liquids allowing omniphobicity. In laboratory studies SLIPS have no toxicity concerns and have extremely low biofilm attachment, outperforming poly(tetrafluoroethylene) (PTFE), nanostructured superhydrophobic, and PEG modified surfaces.[62] Complexity in fabrication, and tailoring towards multiple substrates are concerns for future commercial viability of SLIPS.

Superhydrophobic surfaces inspired by the Lotus leaf effect are also investigated as a potential solution to controlling biofouling. Superhydrophobic coatings are prepared by combining micro/nano-scale roughness with low surface energy surface which allow >150° water contact angles leading to water repellence. Superhydrophobicity is a physical phenomenon due to fewer contact points and trapped air-pockets resulted from surface roughness. This state is commonly known as the Cassie-Baxter state.[63] Anti-fouling performance of superhydrophobic surfaces have been studied although some results suggest a decrease in fouling settlement while some show increased settlement over time.[64-66] The observed trends in fouling settlement is attributed to the size scale of surface features and loss of superhydrophobicity over time. Superhydrophobicity can be lost due to external forces such as pressure and vibrations transitioning from Cassie-Baxter state to Wenzel state (liquid-solid interface). Since marine organism are available in a wide range of size scales, settlement of a certain organism is governed by the size of the features. Scardino *et al* described the attachment point theory where availability of fewer attachment points leads to lower settlement while the opposite is observed for higher attachment points.[67] However engineered nano-silica coatings with persistent superhydrophobicity were developed at University of Melbourne, Australia.[68, 69] These coatings were able to maintain stable trapped air pockets providing persistent superhydrophobicity. Coatings with submicron scale roughness inhibited the settlement/ attachment of diatom (*Amphora coffeaeformis*) attributing to stable air pockets acting as a physical barrier to fouling organisms.[70] However sufficient AF properties were not observed for superhydrophobic surfaces with nano-scale roughness, indicating that fouling inhibition of superhydrophobic coatings depends on size of the air pockets formed rather than their wettability.[70]

A wide range of bio-inspired/biomimetic techniques are currently being investigated as non-toxic alternatives to control biofouling. The potential to combine biomimetic/bio-inspired approaches with current AF/FR technologies make it very attractive to closing in on a practical solution for contending with biofouling. However the ability to reproduce and commercialize these engineered surfaces with a reasonable cost would be the challenge ahead.

Amphiphilic Coatings

The attachment of marine organisms is a complex phenomenon that involves response to surface chemistry, cues, topography, and the surrounding environment.[2] It is known that different species of the same organism respond to the same surface differently making it challenging to come up with coating solutions that work effectively toward the broad range of organisms found in nature.[10, 71, 72] Although the exact mechanism is not fully understood, the primary steps in bioadhesion by marine organisms involve secretion of adhesives consisting of complex proteins and glycoproteins which are amphiphilic in nature.[49] Spreading of these glues is governed by the surface chemistry, wettability and surface-water interfacial interactions. Surfaces with amphiphilic character have shown resistance to protein adsorption. The protein resistant properties are said arise due to surface ambiguity lowering the thermodynamic and kinetic driving forces for protein adhesion.[2, 3, 7] Therefore amphiphilic coatings have been widely explored recently as a non-toxic solution to combat biofouling by discouraging fouling attachment and promote effective fouling release.

A first amphiphilic coating system with surface ambiguity geared towards marine AF was reported in 2004.[73] Complex surfaces with hydrophobic and hydrophilic domains were prepared by combining hyperbranched fluoropolymer (HBFP) and polyethylene glycol (PEG), where surface compositions were tuned by the relative concentration of the two polymer components.[73] When the coatings were exposed to artificial seawater, surface reconstruction was observed which was attributed to the possible swelling of PEG domains providing a micro/nano scale heterogeneous surface.[73] In another study HBFP-PEG coatings showed reduced adhesion of protein lipopolysaccharide and spores of *Ulva*.[74] During this study, the coating with 45% of the PEG component provided the best FR properties towards *U. linza* sporelings.[74] A full scale study was conducted for HBFP-PEG coatings to demonstrate composition tenability, mechanical performance, and anti-fouling properties. These coatings resisted barnacle cyprid settlement, showed 2-3 fold better removal of diatoms (compared PDMS) yet green algae (*U.linza*) adhered strongly.[75] A recent study incorporating PDMS into the coating system still provided nano-complexity and 60% more resistance to protein adsorption compared commercial control.[76]

Mechanically robust non-toxic AF/FR coating systems were developed by having a surface active block copolymer (SABC) layer sprayed (or blended in) onto a poly(styrene-block-ethylene-random-butylene)-block-poly(styrene) (SEBS) thermoplastic elastomer.[72, 77-80] Several amphiphilic coatings were reported based on this coating system which allow to simply modify the surface active polymer layer for tuning surface morphology which in turn affects FR properties. Two species of algae *U.linza* and *N. incerta* (diatom) having opposite adhesion preferences displayed weak adhesion to coatings with amphiphilic SABC modified through grafting ethoxylated-fluoroalkyl side chains compared to SABC with either hydrophilic or hydrophobic side chains alone.[77] Diatoms adhered strongly to surfaces with hydrophobic fluorinated side chain grafted SABC, whereas *U. linza* showed strong adhesion to hydrophilic PEG side chain grafted SABC.[72] Atom transfer radical polymerization (ATRP) allows the control over the composition of SABC synthesis.[80] Compositional variation of amphiphilic SABC on AF/FR properties were studied.[80] The study relieved that increasing PEG composition of the SABC greatly reduced the settlement of *U. linza*.[80] The compositions of SABCs were tuned by changing the density of the fluoroalkyl and PEG side chains to demonstrate the tenability of FR properties.[81] Figure 1.6 shows the trends observed in *U.linza* spore settlement and sporeling removal with respect to compositional variations in SABC. Reduced settlement density of *U.linza* spores and easy removal of sporelings were observed with increasing density of PEG side chains. Also diatoms with opposite adhesion behavior to *U.linza* also showed a similar trend with increasing PEG side chain density. Surface characteristics of the amphiphilic SABC-SBES coatings were studied thoroughly using several surface analysis techniques to understand the surface morphology, rearrangement and wettability which intern affect the AF/FR behavior.[78, 80, 82] Another study was conducted using a thermoplastic base layer with low (almost similar to PDMS) and high young's modulus while having the same amphiphilic SABC layer.[79] Having a lower modulus base layer displayed higher fouling release of grown sporelings of *Ulva* exhibiting effect of modulus on release of adhered marine organisms.[79]

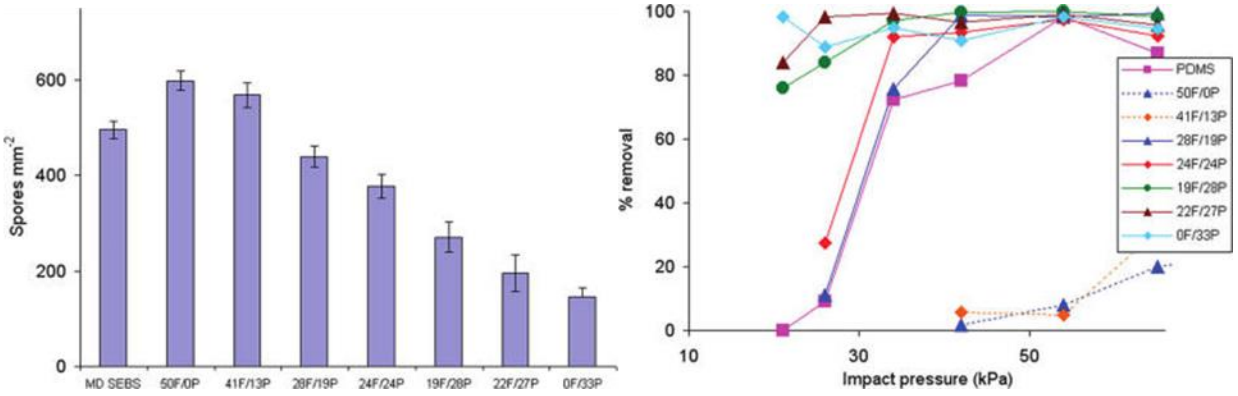

Figure 1.6. Left: settlement densities of spores of *Ulva* on SABCs. Right: percentage removal of sporeling biomass from SABCs. Reproduced from reference [81]

In more recent developments, blending the SABC with the thermoplastic base layer were investigated. During this approach, long and short chain fluoroalkyl side chain were studies for their ability to self-stratify to the surface bringing along the hydrophilic side chains providing an amphiphilic surface. In order to match similar FR performance to previous system (where SABC was sprayed on to SBES), SABC with longer fluoroalkyl side chain was needed.[83] Due to the relatively high cost and the risk associated with environmental resistance of fluorinated materials (compared to PDMS), fluorine-free amphiphilic SABC based coatings were also developed by replacing fluoroalkyl groups with PDMS.[84, 85] Similar fouling resistance/release performance trends were observed for fluorine-free amphiphilic coatings compared to their fluorine containing counter parts. [84, 85] Changing the length of the hydrophilic

PEG segment also affected the AF and FR properties of SABCs.[86] Longer PEG segments improved AF and FR of SABCs towards both algae *N. incerta* and *U.linza*.[86] SABCs modified with amphiphilic segments with non-natural oligopeptides was also reported.[87] The sequence of non-natural amino acid arrangement can result in variety of functionalities and polarities which can be used for optimization of AF and FR properties of coatings.[87] Several different sequences of non-natural peptides were synthesized and attached to the SABC via thiol-ene click reaction and the FR and AF behavior was studied. Interestingly, peptide sequences with large side groups that sterically hinder hydrogen bond donating amides significantly reduced the settlement of *U. linza*.[87] The coatings systems based on the SABC and thermoplastic base layer are a very attractive approach given the fact that surface properties and the modulus can be tuned independently. On the other hand it only requires small amount of the SABC as it is applied as a thin layer thus meeting the criterion for cost effectiveness.

Martinelli *et al.* reported PDMS and amphiphilic acrylic copolymer blends. They synthesized an array of amphiphilic copolymer compositions consisting of varying amounts of poly(ethylene glycol)-fluoroalkyl acrylate (PEGFAA) and polysiloxane methacrylate (SiMA).[88] The amphiphilic copolymer was then blended at various proportions with a PDMS matrix to study the effect of copolymer composition and amphiphilic polymer loading on biofouling. Laboratory bioassays for *U.linza* showed that a copolymer with a 10:90 mole ratio of PEGFAA/SiMA was effective in inhibiting settlement and had higher biomass removal at 1% and 4% concentrations in the PDMS matrix.[88] Similarly, barnacles displayed lower critical removal stress for the same coatings described above.[88] Atomic force microscopy (AFM) showed that the coatings had nano-scale heterogeneity attributed to their amphiphilic nature. Also the coatings with the best performance at laboratory assays displayed comparable FR performance to Intersleek® 700 (commercial FR coating).[88]

An amphiphilic coating system comprised of a silanol-terminated polydimethylsiloxane, a silanol-terminated polytrifluorpropylmethylsiloxane (CF3-PDMS), 2-(methoxy(polyethyleneoxy)propyl)-trimethoxysilane (TMS-PEG), methyltriacetoxysilane and hexamethyldisilazane-treated fumed silica was formulated and studied for FR performance using high-throughput methods.[89] The study suggested that the FR properties towards bacteria (*C. lytica* and *H. pacifica*) and barnacles were improved for coatings with both CF3-PDMS and TMS-PEG.[89] However the diatom (*N.incerta*) FR properties were minimally affected by compositional changes with CF3-PDMS and TMS-PEG components in the formulation.[89]

Poly(ethylene oxide)-silane (PEO-silane) amphiphile (α-$(EtO)_3Si-(CH_2)_2$-oligodimethylsiloxane$_{13}$-block-poly(ethylene oxide)$_8$-OCH_3) incorporated into silicone coatings demonstrated human blood protein resistance (Figure 1.7).[90] Later anti-fouling properties of PEO-silane amphiphile modified silicone coatings were explored.[91, 92] Changing the siloxane tether length of the PEO-silane amphiphiles helped to tune the AF properties toward bacteria (*Bacillus* sp.416) and diatom (*C. closterium*).[92] The highest resistance to bacteria and diatoms were observed for coating which contained the amphiphile with the longest siloxane tether length.[92] Surface force spectroscopy and AFM revealed that the silicone coating underwent rearrangement to bring PEO-silane amphiphiles to the surface explaining the AF properties.[93] In another study, the effect on protein resistance properties of silicone elastomers modified with PEO-silane aphiphiles with varying PEO segment length was studied.[91, 94] Amphiphiles with Longer PEO segments (n=8 and 16 PEO repeat units) were effective at protein resistance.[94] However amphiphile with n=8 PEO repeat units provided protein resistance with a concentration of 10 µmol per 1g of silicone, while the amphiphile with n=16 PEO segment required 25 µmol per 1g of silicone to provide the same level of protein resistance.[94] Using amphiphiles to improve FR performance of silicones is very useful approach given that majority of commercial FR coatings are based on silicone elastomers.

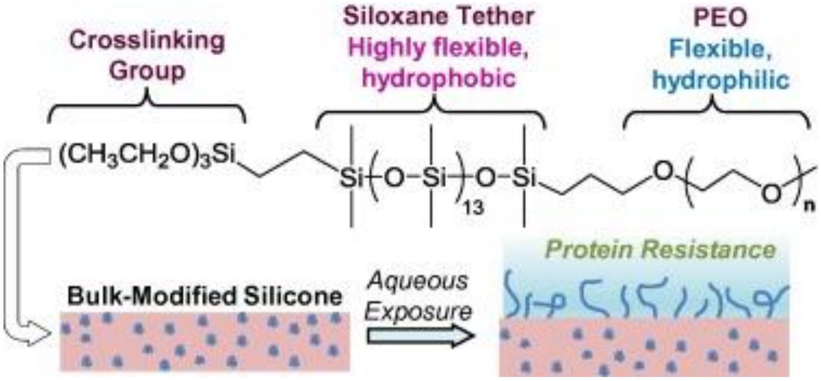

Figure 1.7. Chemical structure of PEO-silane amphiphile (n = 3, 8, and 16) and surface reconstruction of bulk-modified silicone coating with PEO-silane amphiphile. Reproduced from reference [95]

Several different approaches are being explored for preparing amphiphilic coatings for non-toxic marine coatings. Several newly introduced state-of-the-art commercial FR coatings, Intersleek® 900, Intersleek® 1100SR and Hempasil® X3 are said have amphiphilic surface characteristics.[96-98] Significant amount of evidence from published research also support that amphiphilic coatings are more effective in achieving good FR performance towards wide range of organisms with diverse adhesion preferences compared to using strictly hydrophobic coatings. However the same criteria apply for the development of novel amphiphilic marine coatings; they need to be easy to fabricate, provide long term FR performance, require minimal maintenance and be cost effective.

Hydrophilic/ Zwitterionic Coatings

Zwitterionic materials are known to provide protein resistant properties due to the presence of a strongly bonded electrically induced hydration layer.[2] Therefore it is energetically unfavorable for proteins to exclude water molecules from the surface to be adsorbed. Coatings prepared using zwitterionic polymers may offer the added benefit of being low fouling with FR properties. Poly(sulfobetaine) (polySB) and poly(carboxybetaine) (polyCB) are commonly explored zwitterionic polymers with good chemical stability, low cost and superhydrophilicity. [99, 100] Also these polymers can be used to overcome the drawbacks associated with PEG based systems given their susceptibility to pH sensitive degradation.[2] The electrically induced hydration layer is more tightly held compared to that by hydrogen bonding; another advantage of using zwitterionic polymer over PEG based AF coatings.

A fouling-resistant zwitterionic coating was prepared by surface initiated ATRP of poly(sulfobetaine methacrylate) (polySBMA).[101] These coatings showed extremely low settlement of green algae (*U. linza*) spores and diatoms (*N. incerta*) compared to untreated glass.[101] On the other hand, SBMA based coatings showed significantly higher removal of *U.linza* sporelings after water jet treatment at 63 kPa.[101] In another study SBMA and poly(carboxybetaine methacrylate) (CBMA) based coatings provided AF properties towards barnacle cyprids (no settlement over 72 hours on both coatings) although the surface exploration behavior of larvae was different for the two surfaces.[102] A hydrolysable zwitterionic surface based on polyCB was developed.[99] This approach provide a positively charged surface (before hydrolysis) that kills bacteria and releases the residue upon hydrolysis to form a zwitterionic surface which becomes an ultra-low fouling surface.[99] These of zwitterionic polymers for marine coatings is a very interesting strategy since they greatly reduce the settlement of marine organisms. However obtaining appropriate surface density of zwitterionic groups, and developing a practical coating system remain as future challenges.

Research Scope and Purpose

The purpose of this research is to modify the SiPU coating system to achieve improved FR performance through tailoring the surface properties. Ideally the modifications considered should not compromise the mechanical durability of the coating system while having comparable or better FR properties over leading commercial FR standards. This work also hopes to demonstrate that the SiPU coating system is a highly tunable and practical marine coating system that is able to evolve along with improving technology in non-toxic marine coatings research while addressing the drawbacks of silicone elastomer based FR standards.

Preliminary work has been conducted to show improvements to the SiPU coating system with intentions to improve FR properties for broad range of marine organisms. Initial attempts to formulate amphiphilic siloxane-polyurethane (AmSiPU) coatings was reported in 2012.[38] Bodkhe *et al.* prepared two types of amphiphilic siloxane-polyurethane coatings; one AmSiPU system was developed using an amphiphilic carboxylic acid functionalized PDMS (with amine terminal groups) and the other using a PDMS with PEO side chains.[38, 103] Both systems were prepared based on the concept of the self-stratified SiPU system. Surface characterization using contact angle measurements, AFM, confocal Raman, and ATR-FTIR suggested that the coating surfaces demonstrated amphiphilic character. When these coatings were tested against biological laboratory assays for FR properties, AmSiPU coatings with acid functionalized PDMS showed excellent FR of diatoms (*N. incerta*) although critical removal for barnacles were very high (strong adhesion of barnacles).[38] In the case of PEG modified AmSiPU coatings, FR properties of green algae (*U. linza*) was compromised while improved FR properties towards diatoms (*N. incerta*) compared to first generation SiPU coatings without hydrophilic groups.[74] In a similar study, using a zwitterionic SBMA-PDMS-SBMA triblock copolymer provided good FR properties for diatoms, comparable to Intersleek® 900, yet sporelings of *Ulva* adhered strongly showing impaired FR.[104] These previous attempts to develop AmSiPU coating systems show that achieving an appropriate balance of hydrophilic vs. hydrophobic moieties is the key to obtaining effective FR surfaces with FR performance for a broad range of organisms. In order to overcome the shortcomings of the previous studies, surface properties of SiPU coatings needed to be optimized. Thus it led to the work discussed in this dissertation considering various approaches to surface modify SiPU coatings for improved FR performance.

During this research, several approaches were considered to modify the SiPU coatings. The effects on FR performance by incorporating a small amount of phenyl-methyl silicone oil into SiPU coatings were investigated. The mobility of the free silicone oil should provide lubricity to the coating water interface, weakening the attachment of marine organisms, thus improving FR properties. Siloxane-polyurethane coatings with phenyl modified siloxane resins were investigated to understand the effects of phenyl functionality on surface properties and FR performance of SiPU. Field immersion trials were conducted for selected silicone oil modified SiPU coatings. Fouling release properties of coatings prepared by blending amphiphilic acid functional PDMS and PDMS resin were explored with varying compositions. This approach aimed at reducing the hydrophilic acid groups on the coating surface with the intention to improve FR properties towards barnacles. Novel AmSiPU coatings were developed based on amphiphilic polyisocyanate pre-polymers. The coatings were also tested for FR properties along with several commercial standards expecting broad spectrum FR properties. Initial attempts to develop highly hydrated SiPU coatings were also investigated. The presence of a hydration layer may provide improved AF and FR properties to SiPU coatings. Fouling release properties of coatings were evaluated using laboratory biological assays and select coatings were also tested in field immersion trials. Surface characteristics of the SiPU coatings were evaluated using a variety of techniques such as contact angle measurements, AFM, X-ray photoelectron spectroscopy, and ATR-FTIR.

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CHAPTER 2. FOULING-RELEASE PERFORMANCE OF SILICONE OIL-MODIFIED SILOXANE-POLYURETHANE COATINGS

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 2.1).[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]

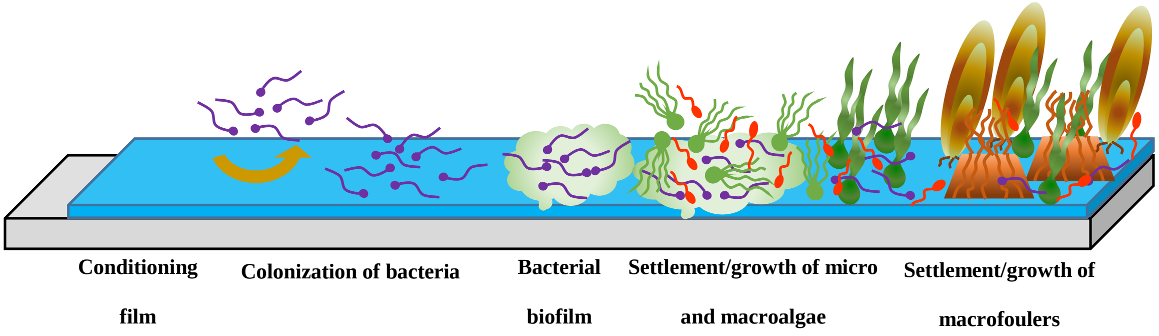

Figure 2.1. Fouling development on a structure submerged in seawater

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 2.1. 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 2.2. 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 2.2).

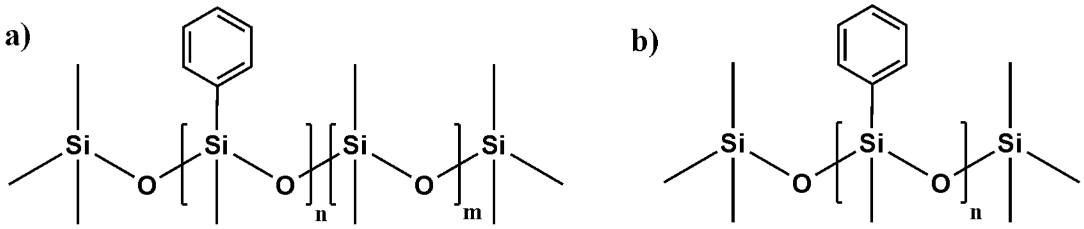

Figure 2.2. Chemical structure of silicone oils used for the experiment. a) phenylmethyl dimethyl siloxane copolymer oil and b) phenylmethyl siloxane homopolymer oil

Table 2.1. 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 2.2 shows all the experimental coating formulations.

Table 2.2. 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

$$100 - \left(\left(\frac{F_r}{F_0} \right) \times 100 \right) \qquad \textbf{(Equation 2.1)}$$

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 2.2) 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 2.3.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 2.3.b 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.

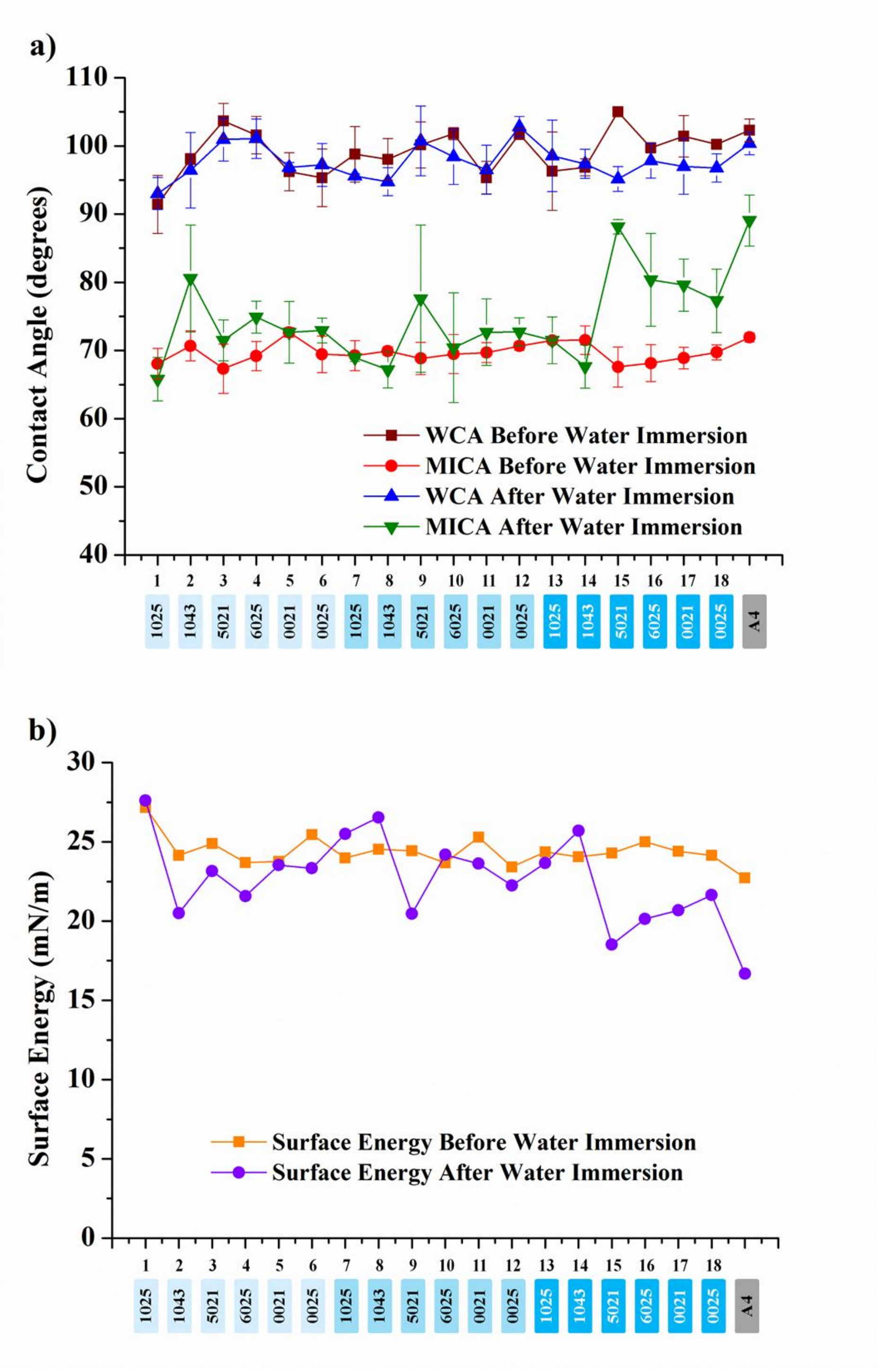

Figure 2.3. a) Water and methylene iodide contact angles before and after 28 days of water aging. Each data point represents the average and standard deviation of 3 measurements. b) Surface energy of coatings calculated by the Owens-Wendt method utilizing the average WCA and MICA measurements. Coatings 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 2.4. (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 2.4.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 2.4.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 2.4.b and 2.4.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.

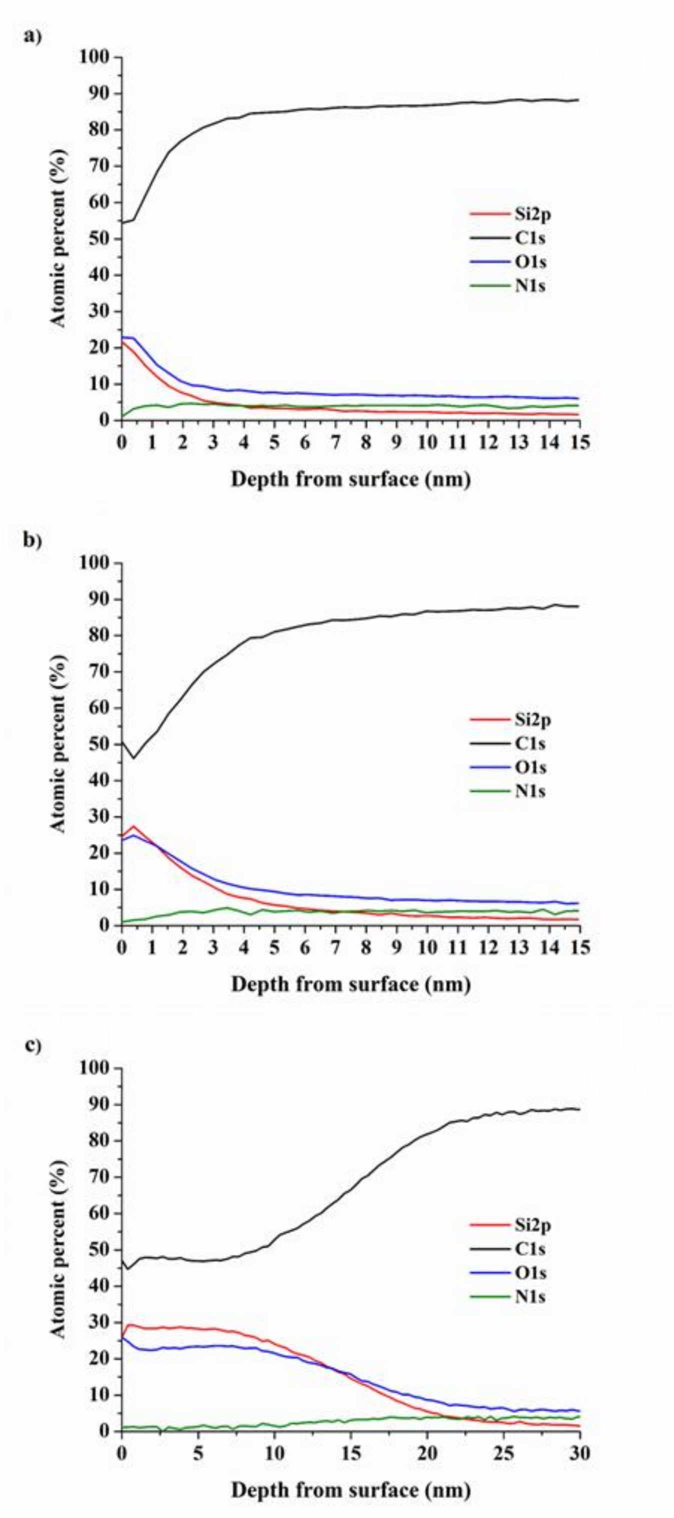

Figure 2.4. XPS atomic concentration depth profile of a) A4-20 siloxane-PU without oil; b) silicone oil-modified formulation 5; and c) silicone oil-modified formulation 17

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 2.5 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 A2 and A5, 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 2.5). 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 A4). 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 A7). 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 A7).

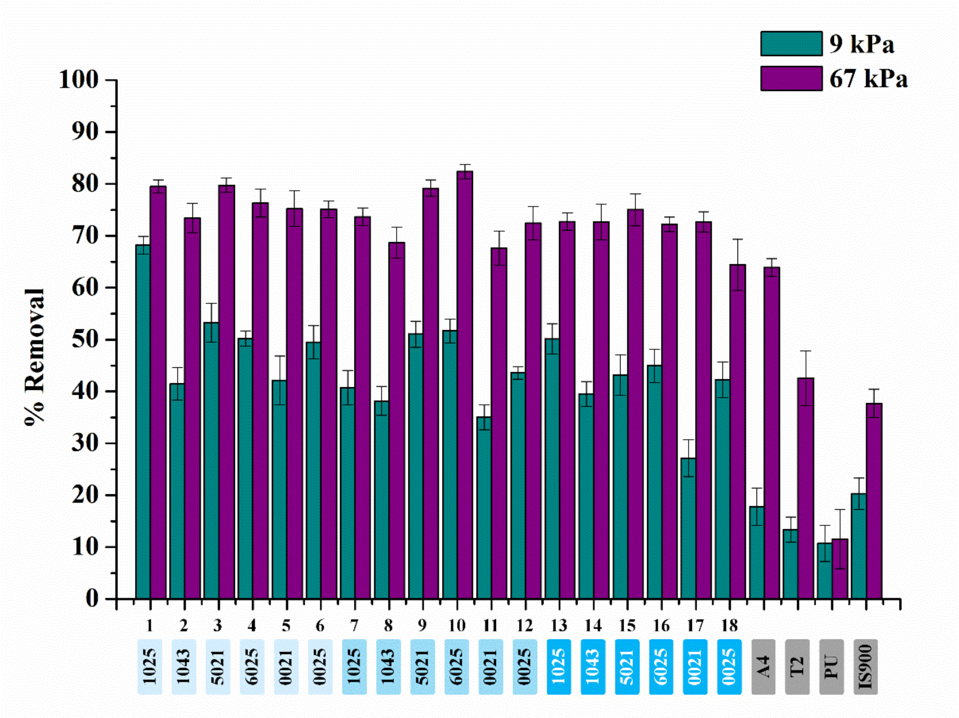

Figure 2.5. Macroalgae (*Ulva linza*) removal from experimental and control/standard coatings after water-jet treatment at 9kPa and 67kPa. Each data point represents the average percent removal value of 6 replicates. Error bars indicate one standard error of the mean. Coatings labels: Coatings are arranged 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 2.5). 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 2.5, and Table A4,A7). 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 2.5). 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 A3 and A6). 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 2.3.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 A3 and A6).

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 2.6). 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 2.3.a and 2.3.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%).

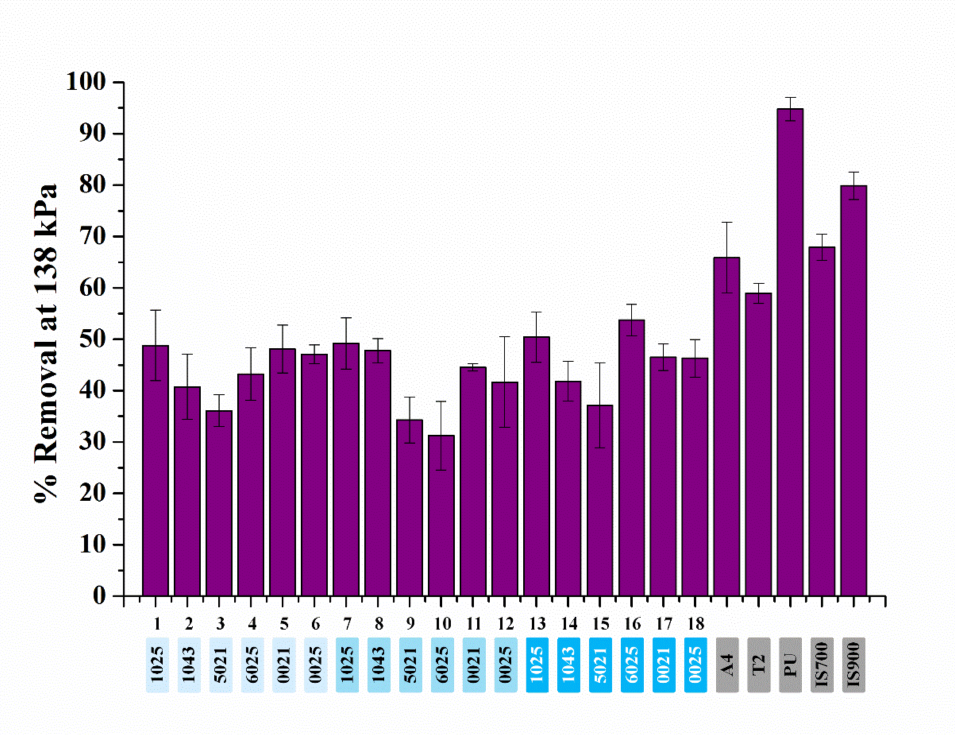

Figure 2.6. Diatom (*Navicula incerta*) removal from experimental and control/standard coatings after treatments with a 138 kPa (20 psi) water jet pressure for 10 s seconds. Each percent removal value represents the average of 3 replicates samples. Error bars indicate one standard deviation of the mean. 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 A8). 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 α=0.05 significance level (Table A9). On the other hand, they also showed comparable performance to Dow Corning T2 silicone elastomer in regard to *N. incerta* removal (Table A9). 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 2.7. 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 A11). 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 A12). 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 α=0.05 significance level, this formulation also outperformed IS 700 (p-value <0.05, Table A12 and A13). 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 A12 and A13). 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.

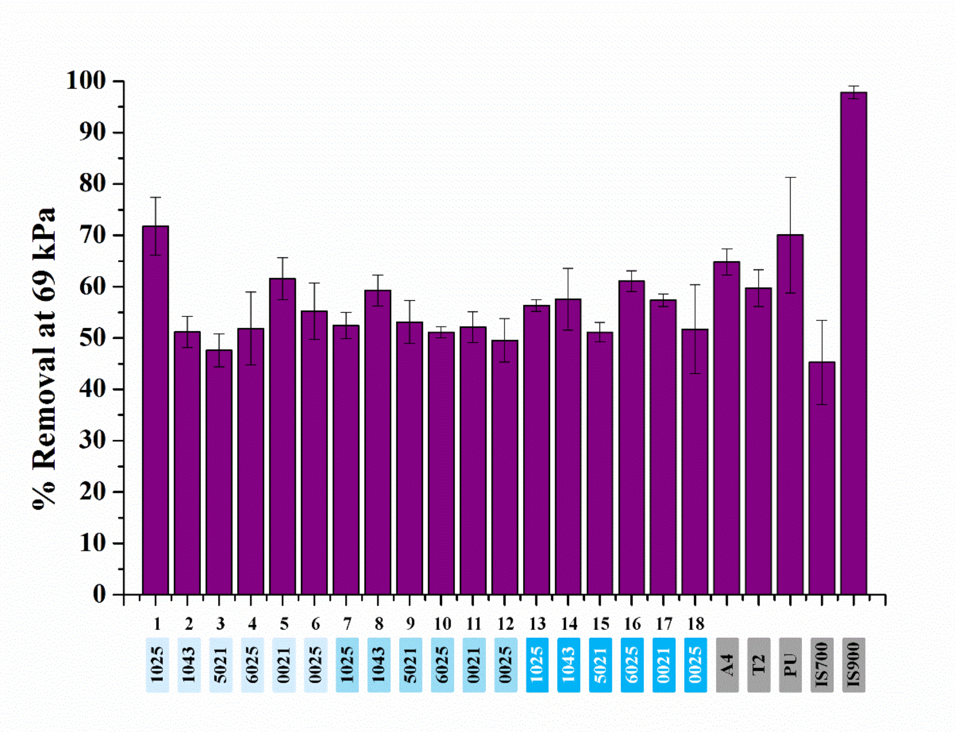

Figure 2.7. Bacterial (*Cellulophaga lytica*) biofilm removal from experimental and control/standard coatings after being exposed to a 69 kPa (10 psi) water-jet treatment for 5 s. The percent removal values represent the average of 3 replicate samples. Error bars indicate one standard deviation of the 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 2.8 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.

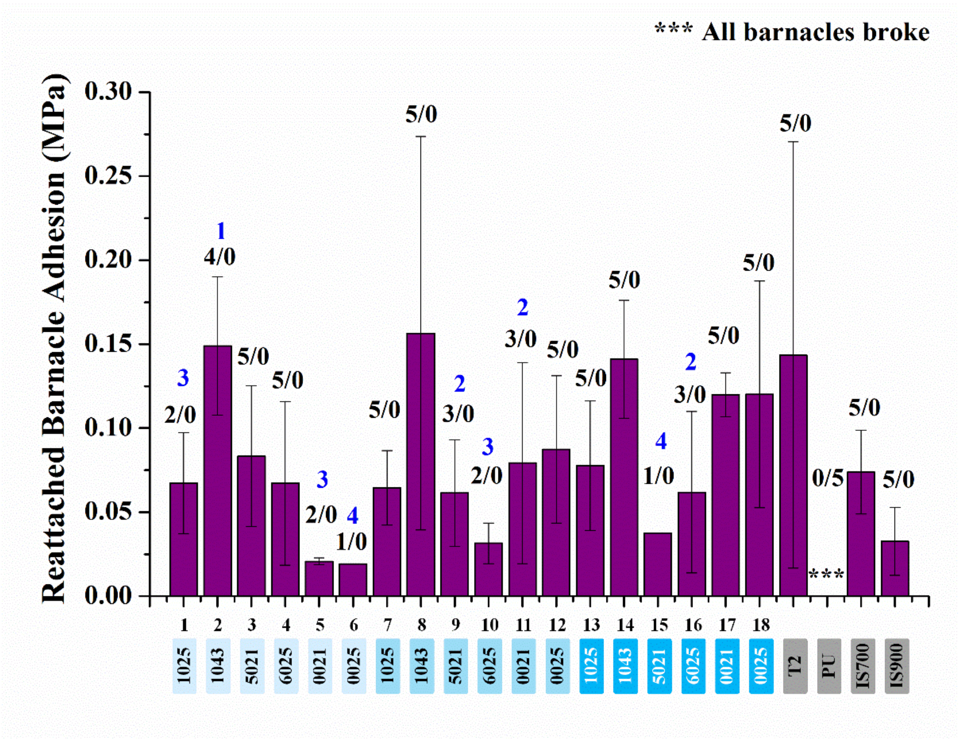

Figure 2.8. Adhesion of reattached barnacle (*Amphibalanus amphitrite*) experimental and control coatings. Five adult barnacle reattachments were attempted for each coating. Each adhesion strength value represents the average of total number of reattached barnacles released without damage. Error bars 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 A14). Barnacle adhesion strengths of several experimental coatings (Table A15; 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 2.9 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.

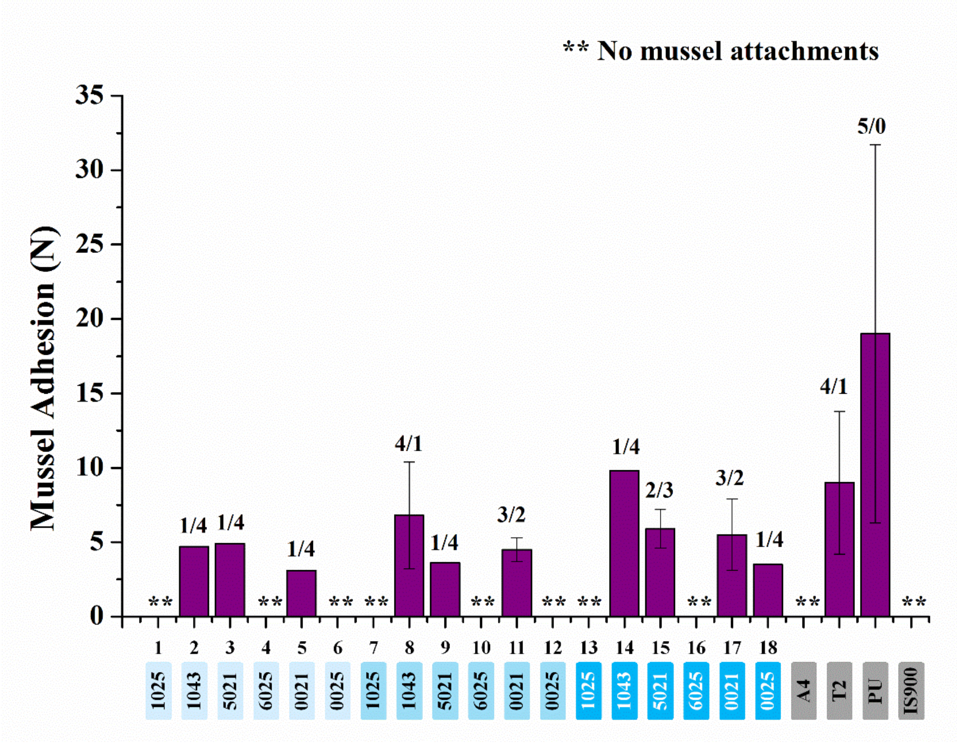

Figure 2.9. Adhesion of mussels (*Geukensia demissa*) to experimental and control coatings. Five mussels were introduced to each coating. Each adhesion strength value represents the average of total number of attached mussels released from the surface. Error bars represent the standard deviation of the 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 2.10 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]

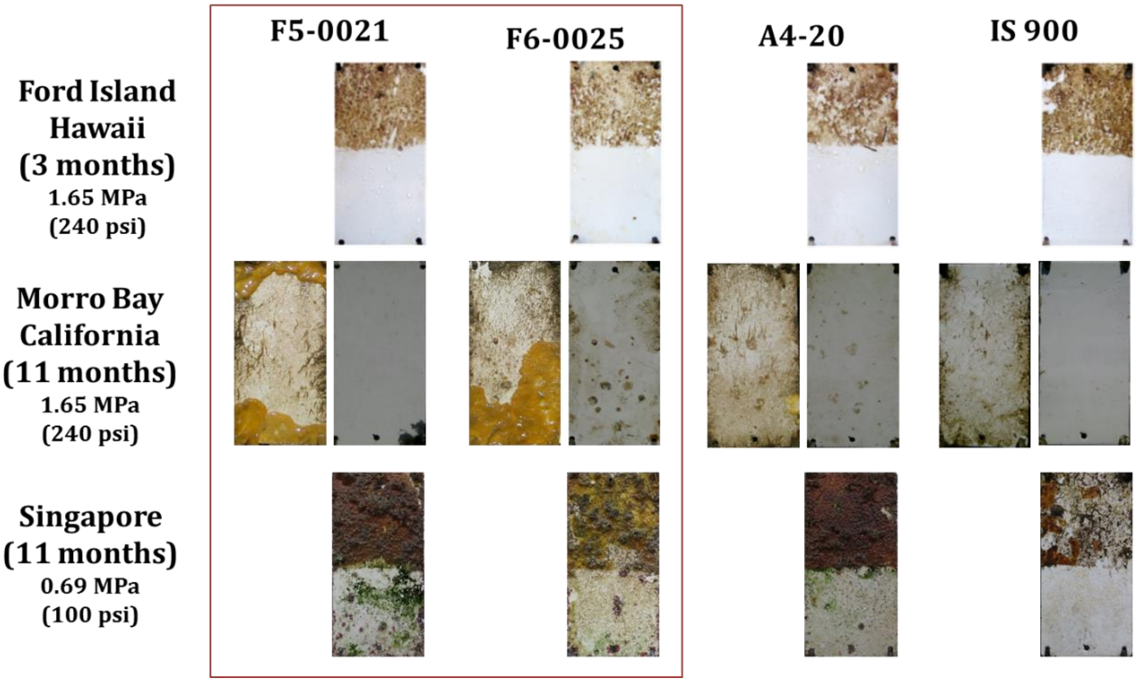

Figure 2.10. Visual appearance of coatings included in field immersion trials at California, Singapore and Hawaii test sites. In Hawaii and Singapore test sites, half of each panel was subjected to water jet cleaning while the other half represents the accumulated fouling. At the California test site, 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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CHAPTER 3. SELF-STRATIFIED SILOXANE-POLYURETHANE COATINGS FROM DIPHENYL-DIMETHYL SILOXANE COPOLYMER; EFFECT OF SURFACE TEXTURE ON FOULING RELEASE PERFORMANCE OF MODEL ORGANISMS.

Introduction

Water repelling surfaces are actively investigated for wide range of applications, from anti-ice coatings, self-cleaning surfaces, microfluidic devices, liquid transport, oil water separation and non-wetting fabrics, etc.[1] Although their use in anti-fouling (AF)/fouling-release (FR) applications have shown promising results towards some marine organisms, obtaining broad spectrum and long term FR performance can be quite challenging.[2, 3] Anti-fouling coatings based on the approach of surface texture and microstructure have been investigated as a potential solution for combating biofouling. Inspired by micro-topography features of shark-skin, research lead by Professor Anthony Brennan at University of Florida developed engineered textured surfaces from polydimethyl siloxane (PDMS) elastomers known as Sharklet AF™.[4-8] Textured and engineered Sharklet AF™ surfaces demonstrated AF properties towards several marine organisms (diatoms, green algae, bacteria and barnacle) in laboratory assays.[6, 9, 10] However the roughness scale and size required for preventing settlement of one particular organism does not necessarily prevent settlement of other organisms. In fact, surfaces that deter barnacle settlement may provide a refuge to green algae spores or vice-versa.[3, 6, 9] Therefore a hierarchical, newer version of Sharklet AF™ surface was developed by superimposing topography that resists *U. linza* spores onto that for barnacle cyprids.[9] However this approach may not be very practical given that the number of identified marine organisms that contribute to fouling has surpassed 4000.[11, 12]

The presence of surface features/texture have been shown to affect the wettability of surfaces. Lotus leaves were one of the famous inspirations adapted from nature to engineer water repellent materials.[1] The observed water repellency of lotus leaves is attributed to its surface microstructure (roughness).[1, 13] Thus the concept of superhydrophobicity is a combination of surface chemistry and surface roughness. Roughened hydrophobic surfaces can provide superhydrophobicity due to trapped air pockets. This concept was explained by the Cassie-Baxter model (Figure 3.1 left), when water comes in contact a solid-air-liquid an interface is formed and the water droplet sits on the air pockets.[14] This stage allows for the minimum contact between the solid and the liquid resulting in spherical water droplets, which can easily roll off the surface. This behavior is commonly known as the lotus effect. However with increasing exposure time and effects of other external forces may disrupt superhydrophobicity resulting in wicking (Figure 3.1 right) which may look more like the Wenzel state.[5] The Wenzel model describes a simpler solid-liquid state where no air pockets are present (Figure 3.1 right).[15] [16] Maintaining superhydrophobic behavior in the marine environment for a long period is the biggest drawback for engineered/textured surfaces for FR applications.[2]

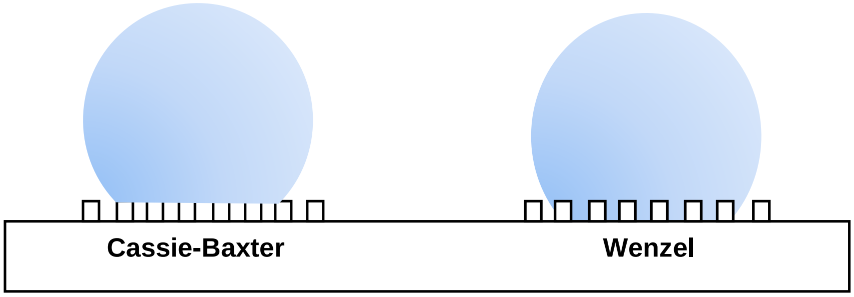

Figure 3.1. Behavior of water on rough surfaces. Left: Cassie-Baxter state where water droplet is sitting on the trapped air pockets. Right: Wenzel state where air pockets were displaced allowing liquid to be in complete contact with the solid

Several studies have reported that phenylmethyl silicone oil has helped to improve the FR properties of PDMS elastomers.[17-20] Surface lubricity and improved stratification of PDMS were cited as the main reasons for observed FR property improvements.[17, 21, 22] Phenylmethyl silicone oils have slightly higher surface tension compared to PDMS which allows effective surface migration of PDMS. [17, 18, 22] Siloxane-Polyurethane (SiPU) FR coatings are a tough and durable approach to combat biofouling.[23, 24] The SiPU coating system combines low surface energy siloxane with polyurethane. During ambient cure, the siloxane self-stratifies to the surface providing FR properties.[25] Improving the FR properties of SiPU coatings is one of the main goals of the work described here. In a previous chapter, phenylmethyl silicone oil modified siloxane polyurethane (SiPU) formulations showed improved FR performance during laboratory biological assays and in field immersion trials compared to those without the silicone oil. In this study, the effect of incorporating a reactive diphenyl-dimethyl siloxane resin into the SiPU system was investigated. The surface tension of the diphenyl-dimethyl siloxane copolymers can be tailored easily by varying the monomer molar ratio during the Ring Opening Equilibration Polymerization (ROEP). Therefore diphenyl-dimethyl siloxane copolymers can be considered for tuning the surface properties of SiPU coatings.

For this study, an aminopropyl terminated, 33% diphenyl- 66% dimethyl containing siloxane copolymer was synthesized (APT-PDPDMS). Then the APT-PDPDMS was blended with APT-PDMS to formulate SiPU coatings. Although it was unexpected, the SiPU coatings with APT-PDPDMS showed unique topographical features which were rarely observed before for SiPU coatings. These surface features were evident from surface scans obtained using Atomic Force Microscopy (AFM). Fouling release performance was evaluated through laboratory biological assays for bacteria (*Cytophaga lytica*), algae (*Navicula incerta* and *Ulva linza*), barnacles (*Amphibalanus amphitrite*), and mussels (*Geukensia demissa*).

Experimental

Materials

Octamethylcyclotetrasiloxane (D_4), octaphenylcyclotetrasiloxane (D_{4Ph}), and bis (3-aminopropyl)-tetramethyldisiloxane (BAPTMDS) were purchased from Gelest, Inc. Benzyltrimethylammonium hydroxide (in 40% methanol), tetrahydrofuran (THF), 2-heptanone, toluene, chloroform-d ($CDCl_3$), 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 unless otherwise specified. An acrylic polyol used for this study composed of 80% butyl acrylate (BA) and 20% 2-hydroxyethyl acrylate (HEA) and synthesized following a procedure reported previously.[26]

Synthesis of Aminopropyl Terminated Poly (diphenyl-dimethylsiloxane) Copolymer (APT-PDPDMS)

In this study 33% diphenyl containing siloxane copolymer was synthesized through ROEP reaction of D_4 and D_{4Ph}, cyclic siloxane monomers (Figure 3.2). First D_4 (129.61 g) and benzyltrimethyl ammonium hydroxide (0.82 g) were combined in a 500 mL single neck round bottom flask. The content was rotary evaporated for about 30 mins (to remove methanol from catalyst solution). The rotary evaporated mixture was added to 4-neck, 500mL round bottom flask containing BAPTMDS (g) and a reaction set up with mechanical stirring, reflux condenser, thermocouple and N_2 purging. The reaction temperature was set to 80 °C and allowed to equilibrate for 4 hrs. After 4 hrs D_{4Ph} (171 g, white powder) was added to the reaction mixture. The reaction was continued further while maintaining the temperature at 80 °C. Overnight the D_{4Ph} has dissolved in the siloxane oligomers and the reaction was allowed to equilibrate for 48 hrs. After 48 hrs, the reaction was heated to 170 °C for 1 hr. The product was collected and characterized using GPC and ^{1}H NMR.

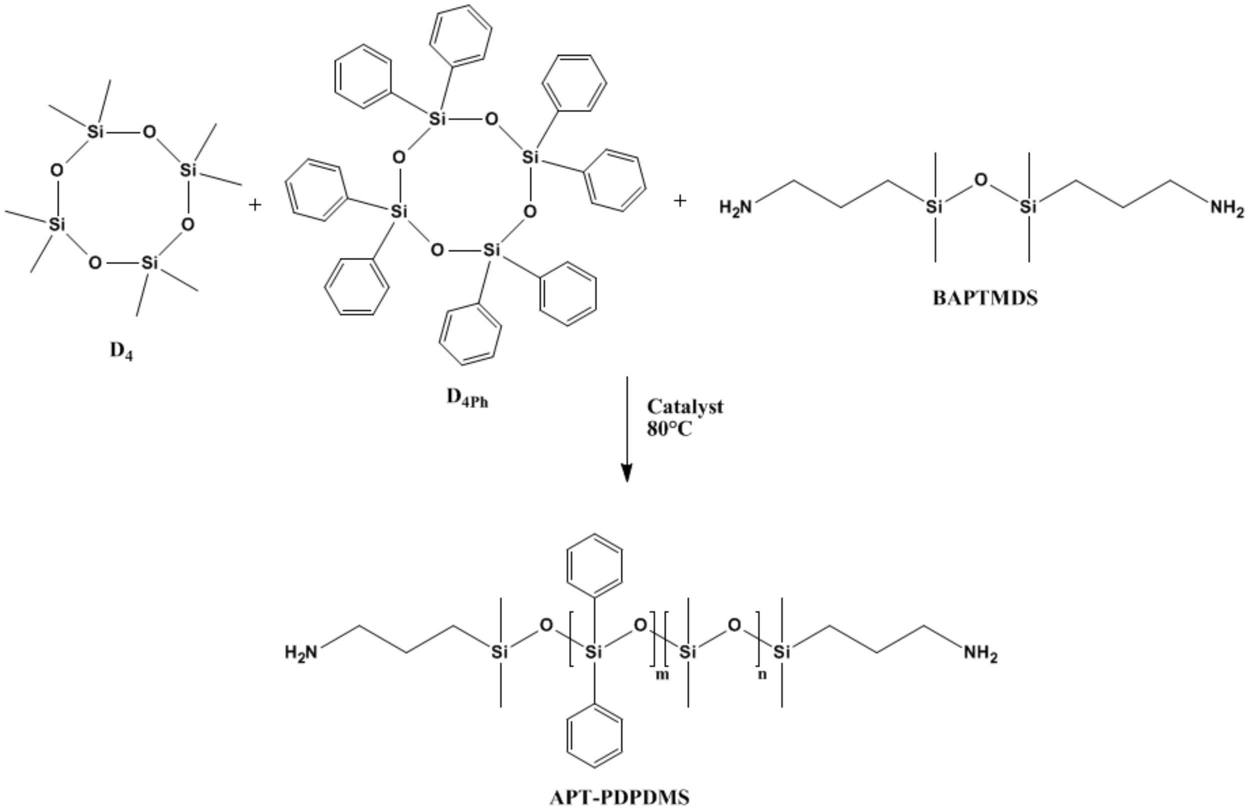

Figure 3.2. Reaction scheme for synthesis of APT-PDPDMS (with copolymer composition, 33% diphenyl-66% dimethyl siloxane)

Synthesis of Aminopropyl Terminated Poly (dimethylsiloxane) (APT-PDMS)

The cyclic siloxane monomer D_4 (200.02 g) and benzyltrimethyl ammonium hydroxide (0.56 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 thermocouple. BAPTMDS (5.01 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.

Gel Permeation Chromatography (GPC)

Molecular weight of APT-PDPDMS was determined using a high-throughput rapid GPC relative to polystyrene standards. GPC samples were prepared by diluting the acetic anhydride derivatized resins in THF solution (approximately 5 mg/mL concentration). 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

^{1}H NMR was utilized to confirm the structure of APT-PDPDMS resin. APT-PDPDMS resin (5 mg) was dissolved in $CDCl_3$ and the ^{1}H NMR spectra was obtained using a JEOL-ECA 400 (400 MHz) NMR spectrometer.

Coating Formulation

Coating formulations were prepared using the phenyl containing siloxane copolymer (APT-PDPDMS), APT-PDMS, acrylic polyol, isocyanate (Desmodur Z4470 BA). Coating compositions investigated during this experiment are outlined in Table 3.1. Here, a representative formulation procedure for coating 6 is outlined. Siloxane resins APT-PDPDMS (3.75 g) and APT-PDMS (1.75 g) were combined with EEP (5.02 g) in a 40 mL glass vial. The content was thoroughly mixed using the vortex for 5 mins. Acrylic polyol (24.60 g) and acetylacetone (2.50 g) were added to the vial. The content was mixed using the vortex followed by magnetic stirring on the stir plate overnight. The next day isocyanate (11.08 g) and catalyst solution (1.25 g) were added to the formulation. The formulation was allowed to mix using magnetic stirring for 1 hr. Then drawdowns were made using a wire-wound drawdown bar on 8”×4” panels and formulation was also deposited into 24 well multi-well plates in which each well was modified with 1” diameter primed aluminum disks. All coatings were cured under ambient conditions for 24 hrs, followed by oven curing for 45 mins at 80 °C.

Table 3.1. Composition of experimental coatings. The percentage indicated for APT-PDPDMS and APT-PDMS is calculated based on total solids of combined SiPU formulation excluding the additives. The percentage indicated for EEP is calculated based on combined solids of siloxane resins

Coating #	APT-PDPDMS (g)	APT-PDMS (g)	EEP (g)	Acrylic Polyol (g)	Pot-life extender (g)	Desmodur Z 4470 BA (g)	Catalyst solution (g)
1	0.00 (0%)	5.02 (20%)	0.00 (0%)	24.61	2.51	11.07	1.26
2	0.00 (0%)	5.01 (20%)	2.51 (25%)	24.64	2.50	11.05	1.25
3	0.00 (0%)	5.01 (20%)	5.05 (50%)	24.61	2.51	11.07	1.26
4	1.26 (5%)	3.76 (15%)	0.00 (0%)	24.62	2.51	11.09	1.25
5	1.25 (5%)	3.76 (15%)	2.50 (25%)	24.67	2.51	11.05	1.26
6	1.25 (5%)	3.75 (15%)	5.02 (50%)	24.60	2.50	11.08	1.25
7	3.82 (15%)	1.26 (5%)	0.00 (0%)	24.62	2.52	11.08	1.25
8	3.79 (15%)	1.26 (5%)	2.50 (25%)	24.61	2.50	11.05	1.26
9	3.75 (15%)	1.25 (5%)	5.02 (50%)	24.63	2.51	11.05	1.25
10	5.00 (20%)	0.00 (0%)	0.00 (0%)	24.65	2.51	11.10	1.31
11	5.09 (20%)	0.00 (0%)	2.50 (25%)	24.60	2.50	11.08	1.25
12	5.07 (20%)	0.00 (0%)	5.07 (20%)	24.60	2.52	11.06	1.25

Preparation of Standard Coatings

Commercial coating standards Dow Corning T2 (silicone elastomer), Intersleek®700, Intersleek®900, and Intersleek® 1100 (AkzoNobel International Paint) were prepared according to manufacturer's specifications to serve as standards. A pure polyurethane formulation without APT-PDMS was also prepared to be included as a standard. All standards were prepared on both primed aluminum panels and in 24-well plates in order to be evaluated along 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 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.[27] Contact angle and SE analysis were performed both before and after water aging.

Atomic Force Microscopy (AFM) was used to study the topography of experimental coatings. A Dimension 3100 microscope with Nanoscope controller was used to scan the surface of 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)

Following 28 days of pre-leaching, a set of multi-well plates were sent to Newcastle University for evaluating FR properties towards *U.linza*. More detailed procedure of the *U.linza* growth and removal assay using high throughput screening can be found elsewhere.[28] Before conducting any analysis, all 24-well plates were equilibrated in 0.22µm filtered seawater for 2 hrs. To each well containing coating, 1 mL *Ulva* spore suspension adjusted to 0.05 OD at absorbance 660 nm (3.3 x 105 spores mL^{-1}) in single strength enriched seawater medium was added. Spores settled on the plates were grown for 6 days inside an illuminated incubator at 18°C with a 16:8 light: dark cycle (photon flux density 45 µmol.m-2.s-1) with renewal of nutrients every 48 hours. Post-settlement, No washing was performed to remove unsettled spores. After 6 days, first row of wells (6) were maintained untouched, which was later used to quantify the biomass generated for each coating. Consequent row of wells on each plate were sprayed using the spinjet apparatus at 111 kPa impact pressure. In order to quantify the biomass, 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 corresponding to 111 kPa water jet treatment was compared with the unsprayed wells (that were used to assess sporeling growth above).

Growth and Release of Microalgae (Navicula incerta)

Fouling release properties of coatings towards microalgae (*N.incerta*) were evaluated through a laboratory assay conducted at NDSU using methods described previously.[29] [30] Following the 28 day pre-leach, 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 in to each well with coating. In order to facilitate cell attachment, the plates were incubated for 2 hrs under ambient conditions. The 1st column of wells (3) were left untreated to be used as a measurement of initial amount of cell attachment. Consequent coating wells were then subjected to water jet treatment, with water jet pressure of 20 psi (138k Pa) for 10 s. Biomass on untreated and treated wells 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 amount of algae biomass present on the coating surface. Percent removal of diatoms was determined using relative fluorescence of non-jetted and water-jetted wells.

Bacterial (Cellulophaga lytica) Biofilm Adhesion

Fouling-release properties of the coatings towards marine bacterium *C.lytica* was performed at NDSU following the procedure outlined previously.[30] [31] 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. Bacteria settlement was facilitated by static incubation of multi-well plates for 24 hrs at 28°C. The first column of wells (3) were untreated and used as the initial bacterial biofilm growth while the next column was treated with water jet treatment at 20 psi (138 kPa) for 5 seconds. Then a 0.3% crystal violet solution in deionized water was used to stain the coating surfaces. The stained crystal violet was extracted using 33% acetic acid solution and eluates were collected from each coating well. The resulting eluates (0.15 mL aliquots) were measured for absorbance at 600nm wavelength. The absorbance values obtained for eluates 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

Adult barnacle reattachment assay described previously was performed at NDSU to evaluate the FR properties of coatings.[32] [33] Coatings prepared on 8 x 4" panels were used for this test following 28 days of pre-leaching. Adult barnacles (~5 mm in diameter) were supplied by Duke University attached to silicone substrates. Barnacles were dislodged from silicone substrate (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). After 2 weeks the reattached barnacles were pushed off in shear. A hand-held force gauge mounted to a semi-automated device was utilized to push off the attached barnacles. The peak force of removal for each barnacle was recorded. Following barnacle was push-off, 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

Mussel adhesion assay was conducted at NDSU using a second set of coatings prepared on 4" x 8" panels. 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 4 cm long acetal plastic rod (product# 98873A105, McMaster-Carr) 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 using a custom designed template where PVC sheets were placed firmly against the plastic rods in order to make sure that the mussels were in direct 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. After the attachment period, 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

The ring-opening equilibration reaction of cyclic siloxane monomers was performed to obtain a higher MW diphenyl-dimethyl siloxane copolymer with aminoalkyl terminal groups. The reaction is a single set process; however for better compatibility, the D_4 monomer needed to be pre-equilibrated for 4 hrs at 80°C before the addition of D_{4Ph} monomer. It was observed that D_{4Ph} displayed better compatibility with pre-equilibrated siloxane oligomers resulting in high MW siloxane copolymers. GPC analysis of APT-PDPDMS revealed that the MW is close to target value of 10000 g/mol (Table 3.2). Figure 3.3. shows the ^{1}H NMR spectrum of the APT-PDPDMS resin. The strong broad peak at 0.1-0.2 ppm indicated the presence of dimethyl siloxane. Also the presence of broad peaks at 7.5-7.8 ppm were indicative of phenyl groups of diphenyl siloxane. By comparing the integrated peak area of protons from phenyl-siloxane peak and methyl-siloxane peak, APT-PDPDMS resin consisted of approximately 30.18% diphenyl-siloxane and 71.68% dimethyl siloxane (the diphenyl:dimethyl-siloxane peak area ratio was found to be 0.41:0.59).

Table 3.2. Average molecular weight for siloxane resins synthesized and used for coating formulations. The number average molecular weight M_n and polydispersity index (PDI) was obtained from GPC analysis

Siloxane Resin	**Co-Functionality**	**M_n (g/mol)**	**PDI**
APT-PDPDMS	Phenyl	7199	1.61
APT-PDMS	-	7224	2.00

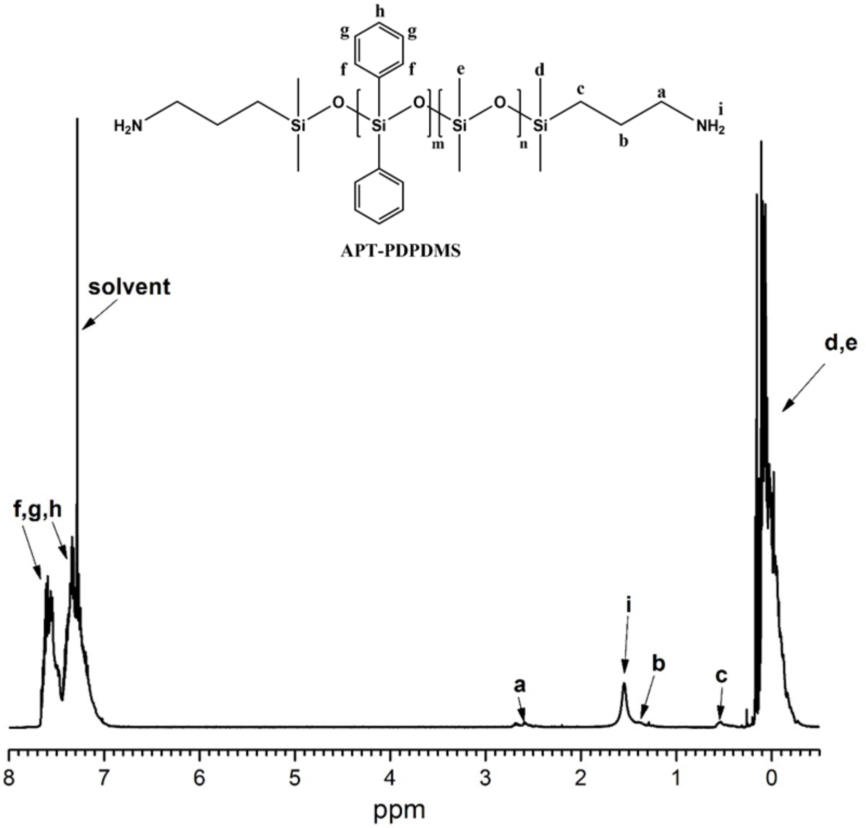

Figure 3.3. ^{1}H NMR of APT-PDPDMS (obtained using a dilute sample in CDCl$_3$) with peak assignments

In order to explore the effect of phenyl content on the performance of the siloxane-polyurethane coatings, a series of coatings were prepared containing mixtures of APT-PDPDMS and APT-PDMS as shown in Table 3.1 In the past, adding EEP has shown to affect the self-stratification of APT-PDMS.[23] Thus varying amounts of EEP were also used to evaluate effects of additional solvent on FR properties. Considering the siloxane resin composition of the formulations, coatings 1-6 have a higher content of APT-PDMS rather than APT-PDPDMS; the opposite relationship is evident for coatings 7-12. In each combination of APT-PDMS and APT-PDMS, coatings with no EEP, 25% EEP, and 50% EEP were included. Figure 3.4 shows the WCAs and MICAs for the experimental coatings following water immersion. The coatings with higher APT-PDMS content (1-6) showed similar WCAs and MICAs after pre-leaching for 28 days, regardless of the variations in solvent (EEP) content. In contrast, the coatings with higher APT-PDPDMS content displayed WCAs above 100°; relatively higher than those for coatings 1-6. Compared to all experimental coatings, coatings 7-9 showed the highest MICAs while coatings 10-12 showed the lowest MICAs. This effect may be attributed to the high amount of APT-PDPDMS interfering with the self-stratification process. Dimethylsiloxane resins have relatively low surface tension (≈22.5 mNm^{-1}) compared to their diphenyl-dimethylsiloxane copolymer resins (≈25 mNm^{-1}). Therefore the presence of APT-PDPDMS in high loading may have caused more of APT-PDMS to migrate to the surface leading to high WCAs and MICAs.

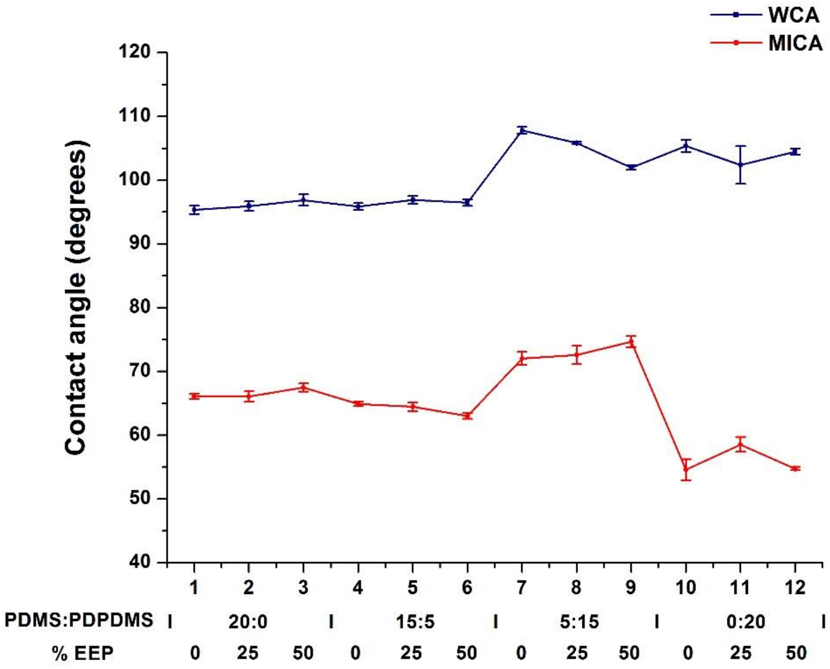

Figure 3.4. Water and methylene iodide contact angles of APT-PDPDMS modified SiPU coatings analyzed following 28 days of tap water immersion. Each data point represents the average contact angle of three replicate measurements. X-axis is labeled in relation to percent wt. ratio of PDMS: PDPDMS and content of additional solvent EEP used to dilute the siloxane blends

The surface energy of the coatings was calculated from the contact angle results (Figure 3.5). Coatings 1-6 had similar SE values suggesting similar surface wettability. However coatings with high APT-PDPDMS content demonstrated some interesting SE values. Coatings 7-9 displayed the lowest SEs (≈22.5 mNm^{-1}) out of all the coatings. Coatings 10-12 showed the highest SEs (≈32.5 mNm^{-1}) out of all the experimental coatings. Since coatings 10-12 did not have any APT-PDMS, these coatings represent SEs similar to surface tension of diphenyl-dimethyl siloxane resins. Whereas coatings 7-9 with 5% of APT-PDMS, lead to coatings with SEs close to surface tension of dimethylsiloxane resins. The contact angle and SE data suggests that using APT-PDPDMS had effects on self-stratification, of APT-PDMS leading to changes in surface wettability. However the addition of EEP did not seemed to affect the contact angles and SE measurements of the coatings.

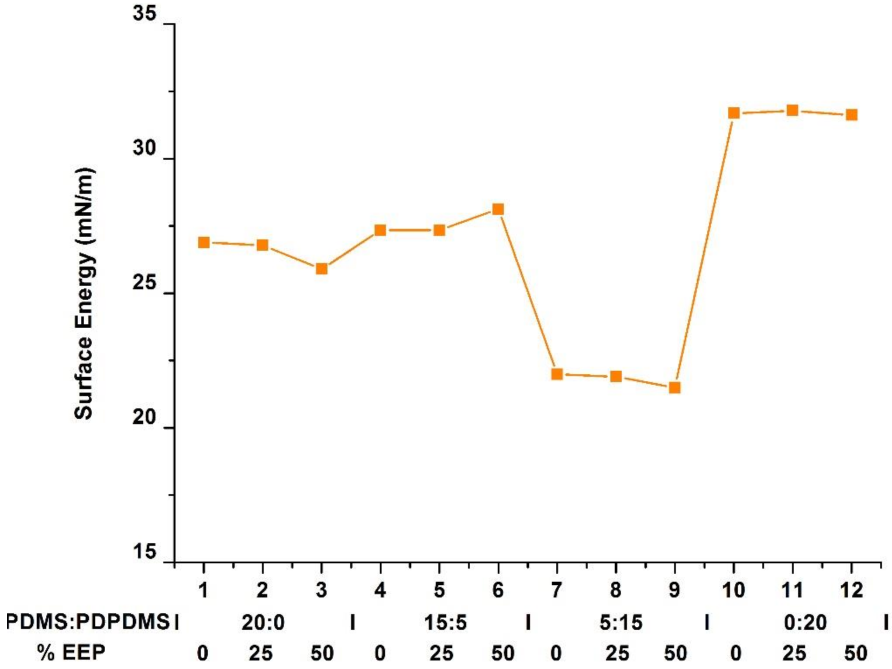

Figure 3.5. Surface energy of APT-PDPDMS modified coatings evaluated following water immersion. Each data point was calculated using the average WCA and MICA for each coating. X-axis is labeled in relation to percent wt. ratio of PDMS: PDPDMS and content of additional solvent EEP used to dilute the siloxane blends

The surface topography of the experimental coatings was analyzed using AFM. Multiple scans of coating surfaces were obtained and Figure 3.6 shows the representative 3D view of height images. It was observed that the SiPU coatings demonstrated interesting topographical features when APT-PDPDMS was introduced. Coatings 1-3 had very smooth surfaces which may be attributed to having no APT-PDPDMS. However coatings 10-12 only containing APT-PDPDMS showed depressions, which are in the size of 15-20µm diameter and uniformly distributed throughout the coating surfaces. Phenyl groups typically introduce more hydrocarbon content to silicone resins which enables the tuning of their surface tension. Phenyl modified siloxane resins have surface tension of 24-30 mN/m. Therefore observed surfaces features of coatings 4-12 may have resulted due to blending the APT-PDPDMS resin with APT-PDMS. Interestingly, the blending ratio of 5: 15 PDMS to PDPDMS resulted in coatings with protrusions (coatings 7 and 8). Due to slight difference in surface tension of APT-PDMS vs. APT-PDPDMS, dimethylsiloxane preferably migrated to the surface minimizing the surface energy. This rearrangement may have led to spike like surface features. Additionally results observed for contact angle and SE measurements were in agreement with variation in surface features observed through AFM imaging.SE

Although addition of EEP did not seemed to affect the contact angle and SE of phenyl modified coatings, surface topography of phenyl modified coatings showed some interesting trends. In general, increasing EEP content resulted in more uniform sized and fairly well spaced surface features for APT-PDPDMS modified coatings. The solvent EEP has a high boiling point (169 °C) and low evaporation rate (0.12, relative to 1 for butyl acetate) compared other solvents used in the SiPU formulation. Slow evaporation of EEP during curing process my allow solvent-polymer interactions leading to changes in surface morphology of coatings. Previous studies show that solvent-polymer interactions of polystyrene-b-PDMS under different vapor pressure affect the size and scale of surface domains.[34]

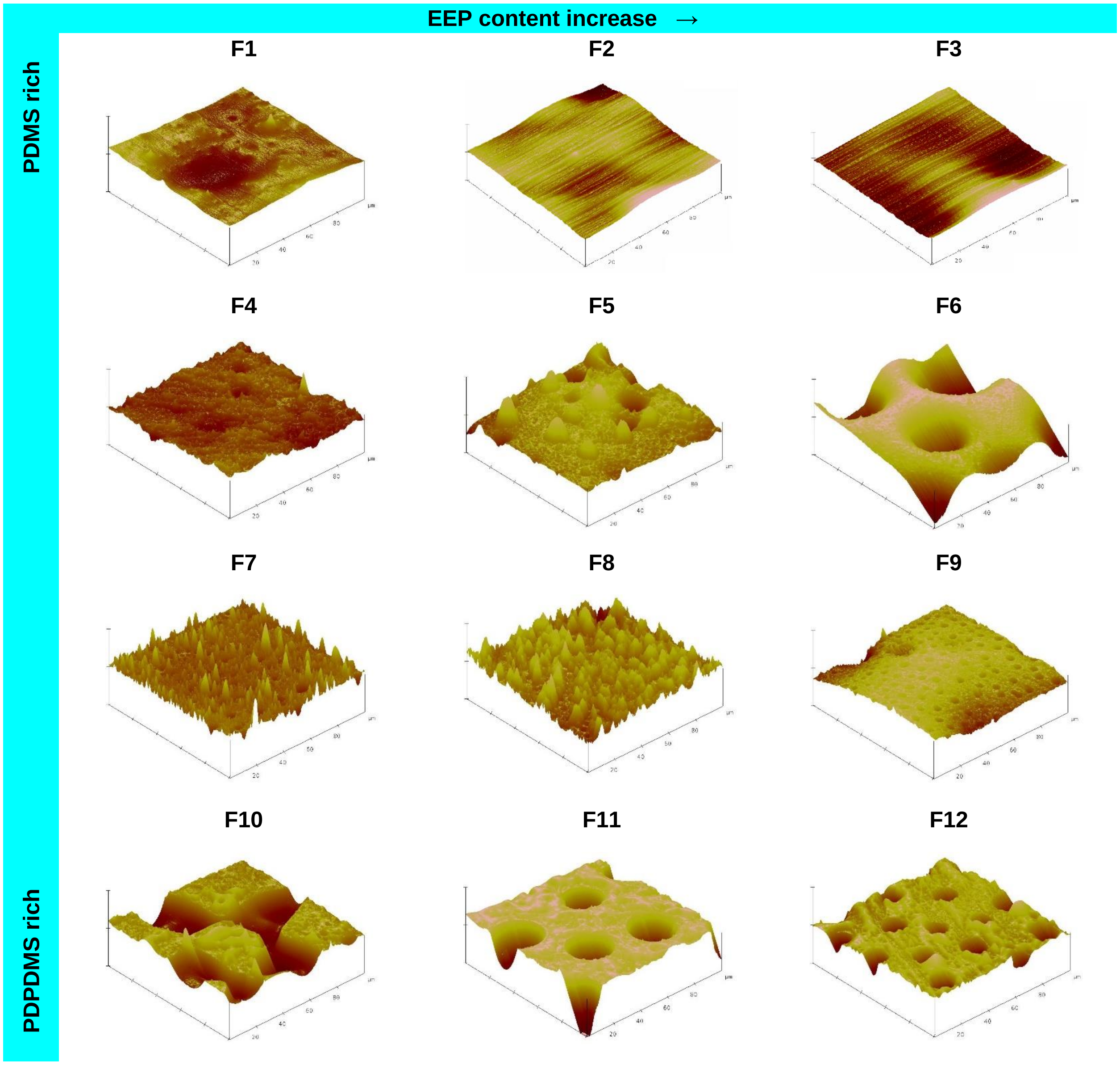

Figure 3.6. AFM height images of APT-PDPDMS modified SiPU coating surfaces after water immersion. For each coating surface area of 100µm×100µm was scanned in the tapping mode. The darker shade indicate depth while the lighter shade indicate height. The horizontal and vertical scales are labeled every 20µm

Figure 3.7 shows the removal of *U. linza* sporelings from coatings. The coatings with high APT-PDPDMS content showed low removal of *U. linza*, whereas coatings with high APT-PDMS content showed high sporeling removal. It has been reported previously that *U. linza* respond to a variety of cues including surface wettability and topography.[35] Surface features such as depressions and corners which were similar or larger than the size of *Ulva* spores tend to provide shelter from hydrodynamic forces.[4, 5, 36]

Also micron scale surface features allow additional surface area for adhesive to spread.[37] In this study, surface features were observed for coatings with APT-PDPDMS. Surface features were quite large for coatings with 20% APT-PDPDMS which explains the observed decrease in fouling-release properties towards *U. linza* sporelings. Coatings 10-12 displayed surface features in the size range of 10-20 µm and thus showed the worst FR efficiency of green algae. Several experimental coatings displayed better FR properties towards *U. linza* compared to PU standard coating yet similar in performance to T2 standard coating. A clear trend for *U.linza* FR properties of SiPU coatings were not observed with respect to the effect of additional solvent EEP. Coating 12 with 20% by wt. APT-PDPDMS and 50% EEP showed the worst *U.linza* FR performance while Intersleek® 1100 standard coating showed the best FR performance with >90% removal of grown sporelings.

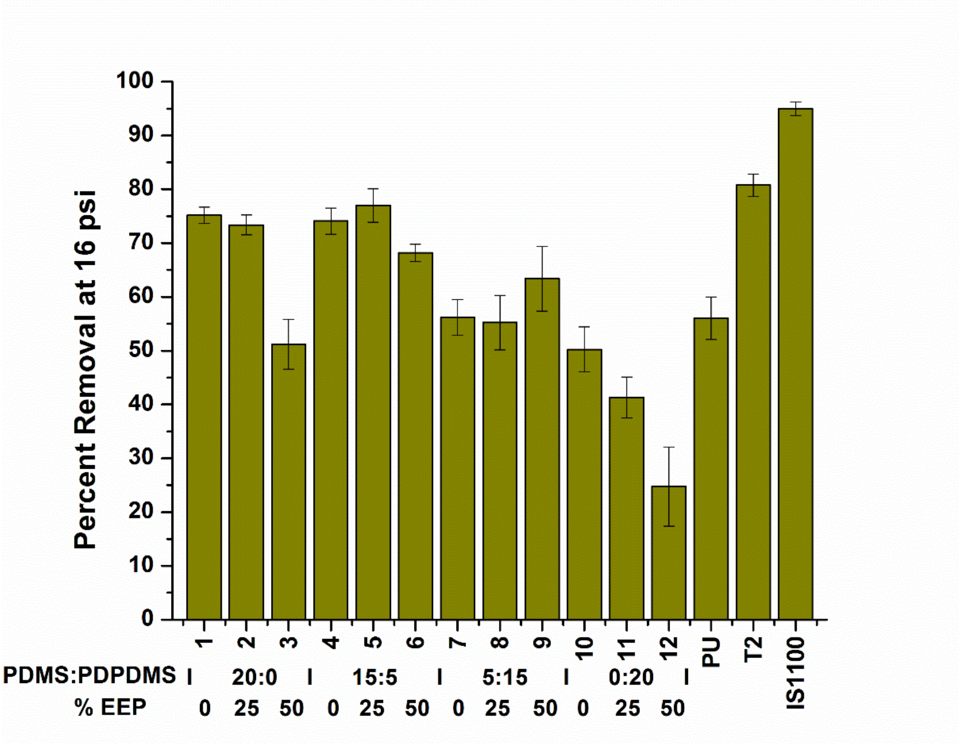

Figure 3.7. Removal of *U. linza* sporelings from coatings following water jet treatment at 111 kPa (16 psi). Each bar represent the average percent removal of 6 replicate measurements. X-axis is labeled in relation to percent wt. ratio of PDMS: PDPDMS and content of additional solvent EEP used to dilute the siloxane blends

Diatom (*N. incerta*) are microalgae which contribute to forming slime on ship hulls. When in contact with a surface, *N. incerta* secrete an adhesive which surrounds the cell and wets the surface.[38] Also previous studies show a reduction in *N. incetra* cell viability for hydrophobic surfaces.[39] Several experimental coatings had very poor FR properties towards diatoms (Figure 3.8). In terms of FR performance during the diatom assay, coating 1-3 with APT-PDMS were slightly better than the coatings with APT-PDPDMS. Diatoms have shown to adhere strongly to hydrophobic surfaces.[39] In previous studies they also displayed stronger adhesion towards surfaces with high coefficient of friction.[38] All experimental coatings were fairly hydrophobic and several surfaces demonstrated surface features. Observed poor FR performance towards diatoms may have resulted by the combined effect of hydrophobicity and high surface roughness due to surface depressions and spikes. However Intersleek® 900 commercial standard showed far superior FR properties compared to all of the experimental the coatings.

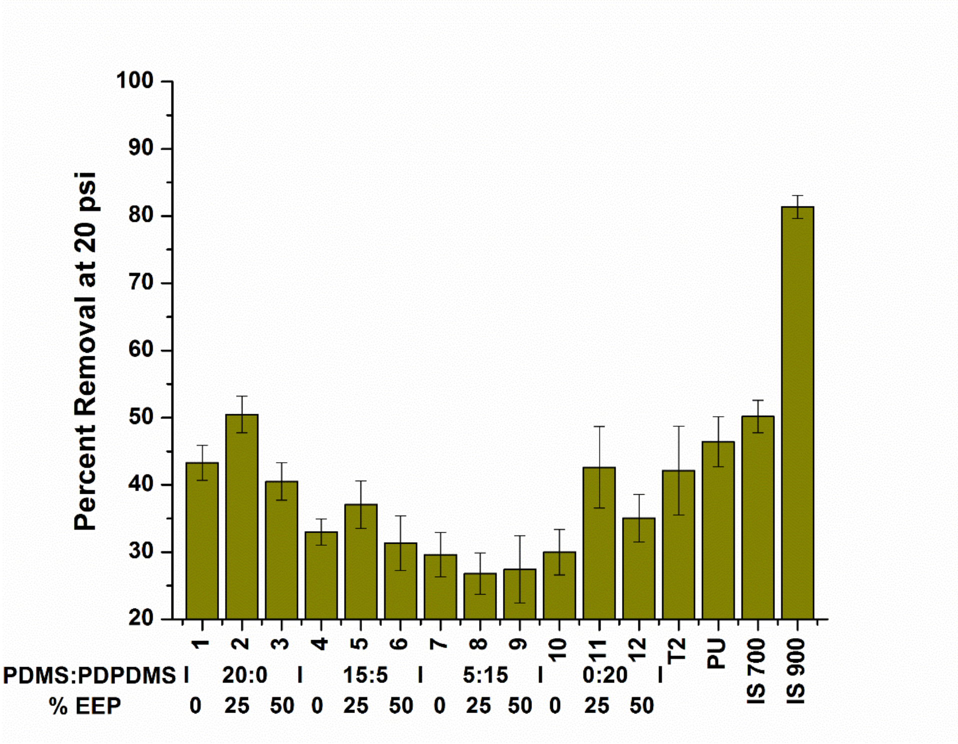

Figure 3.8. Removal of diatom (*N. incerta*) from coatings after water jet treatment at 20 psi pressure. Each bar represents the average percent removal of 3 replicate measurements. X-axis is labeled in relation to percent wt. ratio of PDMS: PDPDMS and content of additional solvent EEP used to dilute the siloxane blends

Although limiting the colonization of bacteria does not necessarily prevent macro-fouling, several studies have indicated that the presence of bacteria may influence the attachment of larvae and spores of other marine organisms.[40] Fouling-release properties towards marine bacteria were evaluated using a retention and retraction assay. Figure 3.9 shows the removal of biomass after water jet treatment at 20 psi. Coatings with a high content of APT-PDMS (1-6) displayed better bacterial biofilm removal compared to standards T2, PU and Intersleek® 700. Coatings 7-12 showed comparable FR properties of *C. lytica* compared to commercial standard Intersleek® 700. However Intersleek® 900 had 87% of bacterial biofilm removal, slightly edging over coatings with 20 wt. % of APT-PDMS (1-3). Overall increasing the content of APT-PDPDMS had resulted in lower removal of *C. lytica*. Having additional solvent EEP does not seems to affect the FR properties of bacterial biofilm significantly.

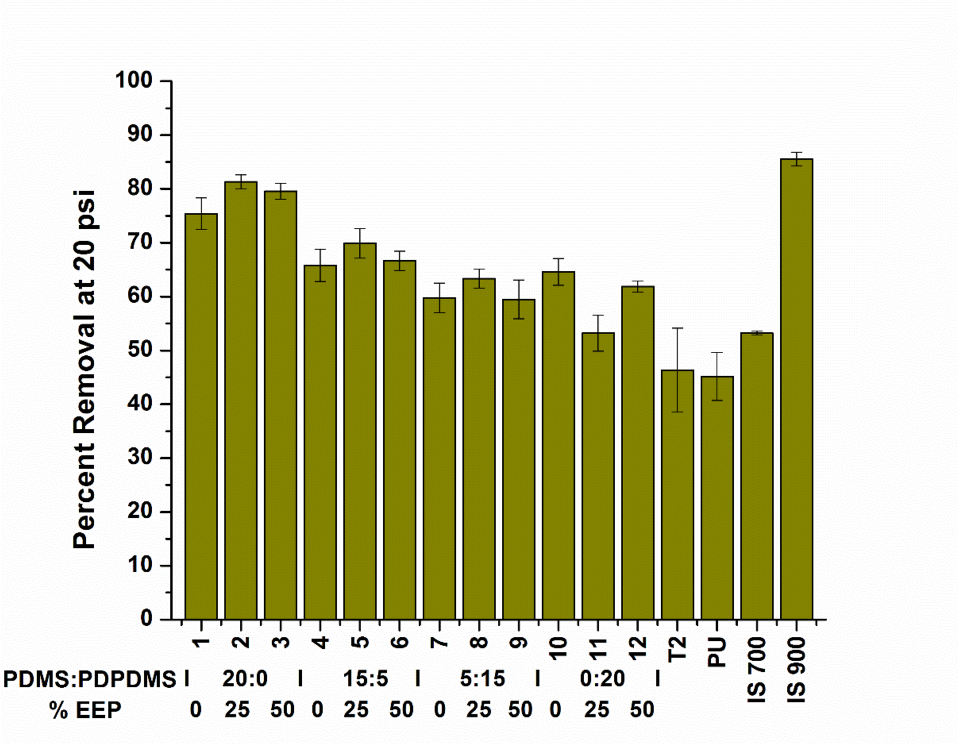

Figure 3.9. Percent removal of bacterial biofilm (*C. lytica*) from coatings after water jet treatment at 20 psi pressure. Each bar represents the average percent removal of 3 replicate measurements. X-axis is labeled in relation to percent wt. ratio of PDMS: PDPDMS and content of additional solvent EEP used to dilute the siloxane blends

Barnacles are macro-fouling organisms that have a significant contribution to biofouling on ship hulls. The release performance of barnacles from experimental coatings was evaluated using a barnacle reattachment assay. Figure 3.10 shows the adhesion strength of barnacles for the coatings from this study. It was interesting to notice that coatings with high APT-PDMS resin content (1-6) displayed comparable release of barnacles as Intersleek® 900 standard. On the other hand coatings prepared with 20% by wt. APT-PDPDMS had high barnacle adhesion strength and several broken/damaged barnacles suggesting poor FR properties. However coatings 7-9 (with 5: 15 blend of APT-PDMS to APT-PDPDMS) showed some interesting results with varying EEP content. Coating 7 with no EEP displayed higher adhesion strength of barnacles compared to coating 9 with 50% EEP (coating 9 had similar performance to Intersleek® 900), while coating 8 displayed anti-fouling behavior towards barnacles. The observed trend may be related to the surface textures observed for coatings 7-9. Previous studies report that barnacle cyprids are sensitive to engineered textured surfaces.[9, 41] In the past, Sharklet AF^{TM} surfaces with 40 mm feature height and an aspect ratio of 2 have shown to reduce *Balanus amphitrite* cyprid settlement by 97% compared to a smooth PDMS surface.[9] Therefore the aspect ratio for features on coating 8 (aspect ratio of 1-2, obtained from AFM cross-section) might be optimal for mitigating barnacle attachment, although the same coating may provide refuge to smaller sized micro-organisms such as diatoms.

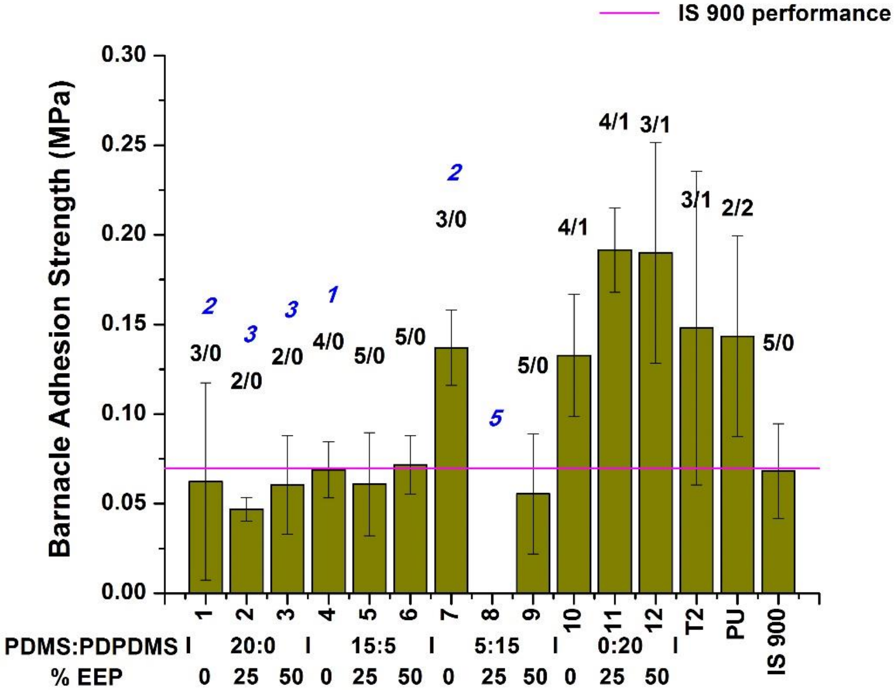

Figure 3.10. Adhesion strength of reattached barnacles (*A.amphitrite*) for coatings. Five adult barnacle reattachments were attempted for each coating. Each adhesion strength value represents the average of total number of reattached barnacles released without damage. The ratio represent the number of measured barnacles over the number of broken/damaged barnacles. X-axis is labeled in relation to percent wt. ratio of PDMS: PDPDMS and content of additional solvent EEP used to dilute the siloxane blends

Mussels are another fouling organism that abundantly attaches to surfaces exposed in the marine environment. Therefore mussel FR properties of coatings were also evaluated (Table 3.3) at NDSU. All experimental coatings displayed resistance to settlement (adhesion) of marine mussels during the 3 day experiment. This result was consistent with results observed for commercial standard Intersleek® 900. Standard coatings T2 and PU had several mussels attached to the coating and they required 8-16 N force for removal.

Table 3.3. Adhesion strength 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 released mussels from the surface

Coating	**Attached mussels**	**Average force for removal (N)**	**Non-attached mussels**
1-12	0	-	6 /each coating
T2	5	8.2±4.7	1
PU	6	15.5±14.5	0
Intersleek® 900	0	-	6

This study has shown that increasing the APT-PDPDMS content resulted in the formation of surface microstructures for many of the experimental coatings. The observed FR properties showed a strong relationship to the surface topographical features and their size scale. Multiple studies suggested the settlement of organisms was greatly influenced by the scale and size of surface features. If the features were bigger than the organism they preferably settle on those surfaces and wise-versa. Coating 8 with spike like surface features, deterred barnacle attachment yet, displayed the worst FR properties towards diatoms and bacteria. All the experimental coatings deterred settlement of marine mussels which was comparable to Intersleek® 900.

Conclusions

Phenyl modified coatings were prepared by incorporating diphenyl-dimethyl siloxane copolymer in a self-stratifying SiPU system. Experimental coatings were hydrophobic and coatings with high APT-PDPDMS resin resulted in higher WCA compared to other coatings. Coatings 7-9 had the lowest SE out of all the coatings. AFM experiments revealed that several experimental coatings displayed surface features following water aging. A combination of surface texture and surface chemistry have a direct relationship to observed FR properties. Using APT-PDPDMS impaired the FR properties of SiPU coatings towards *N. incerta*, *C. lytica* and *U. linza*. However having APT-PDPDMS incorporated in SiPU system lead to anti-fouling properties towards macro-fouling organisms. Coating 8 did not allow any barnacles to reattach to the surface, outperforming all standards including Intersleek® 900. Interestingly, none of the experimental coatings allowed any mussels to attach displaying anti-fouling properties. Overall, the results suggest that incorporation of the diphenyl-dimethyl siloxane copolymer negatively affected the FR properties towards micro-foulers yet lead to anti-fouling behavior towards macro-foulers. This study demonstrated that surface texture dependent anti-fouling/FR solution may not be a practical solution given the number of marine organisms and their complex adhesion profiles.

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CHAPTER 4. 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.[7-9] However non-toxic fouling-release (FR) coatings have gained the most recent interest in research and development of marine coatings.[10-12] 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 better understanding of adhesion processes of marine organisms have allowed continued development of non-toxic FR coatings.[14-16]

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.[17-19] 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. [23-27]

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 bacteria adhesion, SAM surfaces with COOH moieties showed low biomass generated compared to surfaces modified with hydrophobic groups (CH3).[30] However the behavior/ response of two different strains of bacteria were significantly different.

Siloxane polyurethane (SiPU) marine coatings are a practically sound approach to a tough and environmentally friendly FR solution.[31-34] 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

Octamethylcyclotetrasiloxane (D_4), 3-Aminopropyl terminated polydimethyl siloxane having a number average molecular weight of 875 (APT-PDMS-875), 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 4.1). 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 ^1H NMR to confirm the successful synthesis.

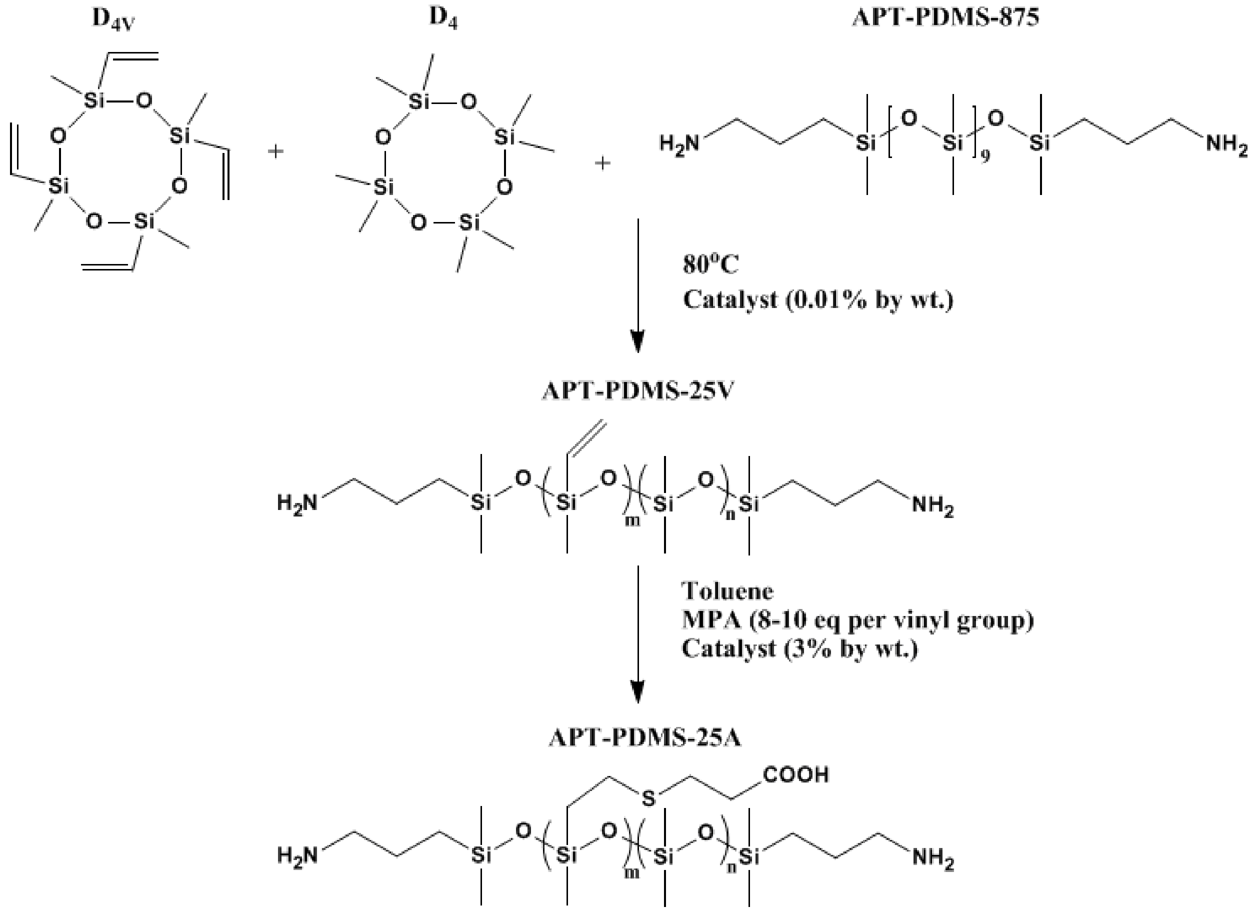


Figure 4.1. Reaction scheme for the synthesis of APT-PDMS-25A

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 separotory 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 solution derivatized with acetic anhydride (approximately 5 mg/mL concentration) 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 4.1. 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 4.1. 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 water contact angle (WCA) and methylene iodide contact angle (MICA) for all experimental coatings. Three measurements of each liquid were obtained using First Ten Angstroms^{TM} 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 4×10^5 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 4.2). ^{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 4.2). 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 4.1. 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 4.2. 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

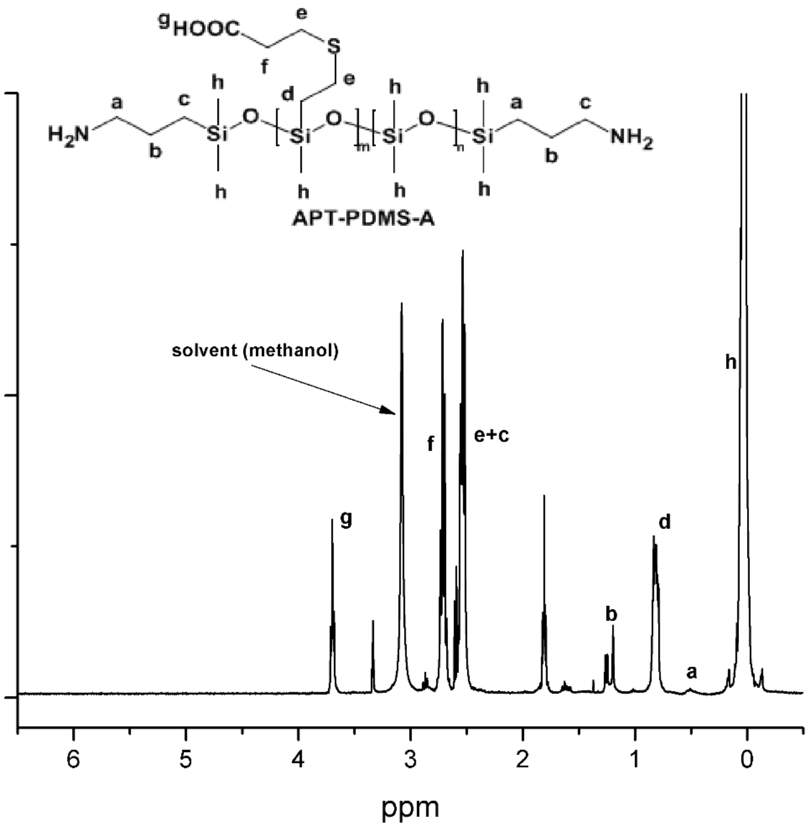


Figure 4.2. ^{1}H NMR of APT-PDMS-25A in solvent (80:20 mixture of $CDCl_3$: methanol-d)

Considering the coating compositions, the first 3 experimental coatings are APT-PDMS-25A rich whereas last three are APT-PDMS rich. Figure 4.3 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.

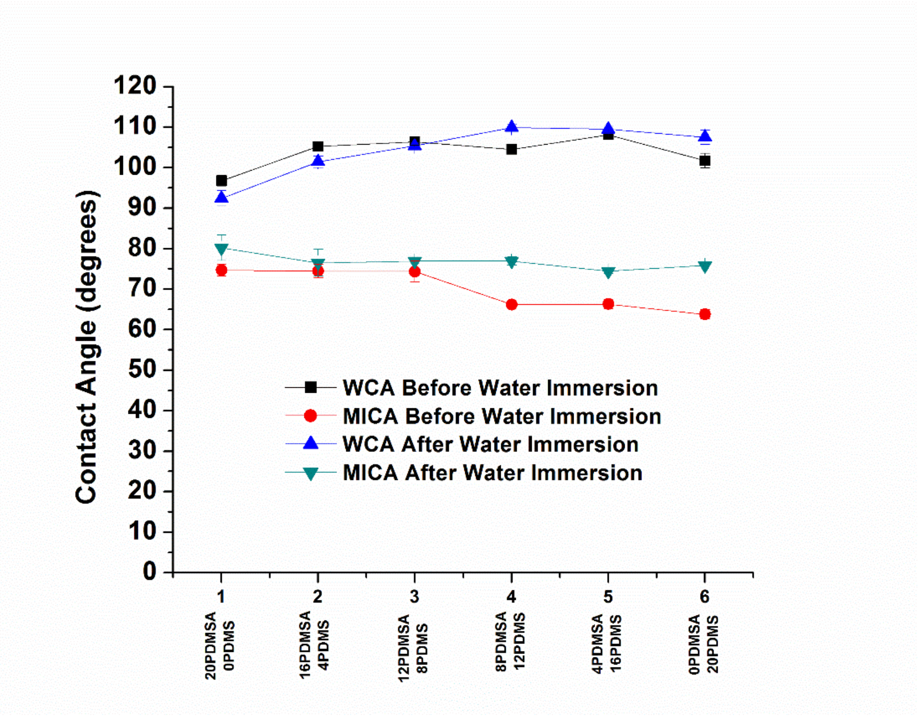


Figure 4.3. Water and methylene iodide contact angles of APT-PDMS-25A modified SiPU coatings analyzed before and after 28 days of tap water immersion. Each data point represents the average contact angle of three replicate measurements

Figure 4.4 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.

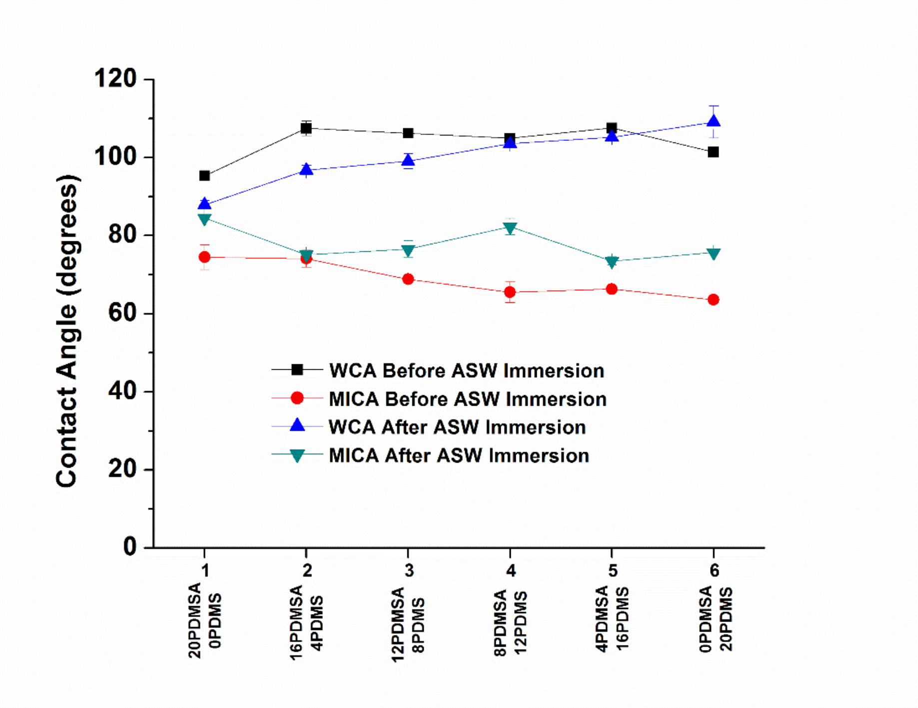


Figure 4.4. Water and methylene iodide contact angles of APT-PDMS-25A modified SiPU coatings analyzed before and after 28 days of ASW immersion. Each data point represents the average contact angle of three replicate measurements

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.

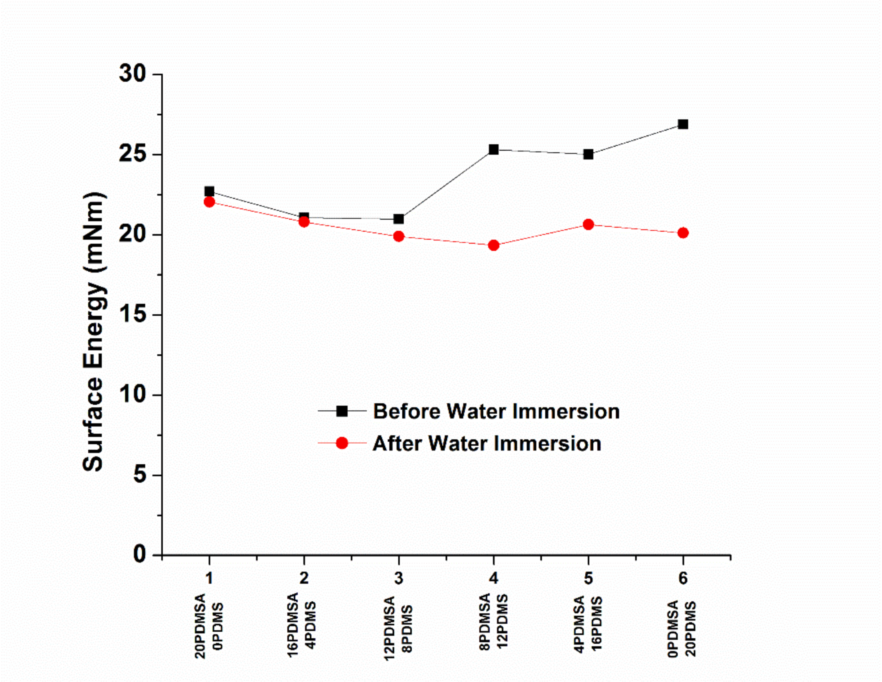


Figure 4.5. Surface energy of experimental coatings evaluated before and after water immersion. Each data point was calculated using the average WCA and MICA for each coating obtained from water aging study

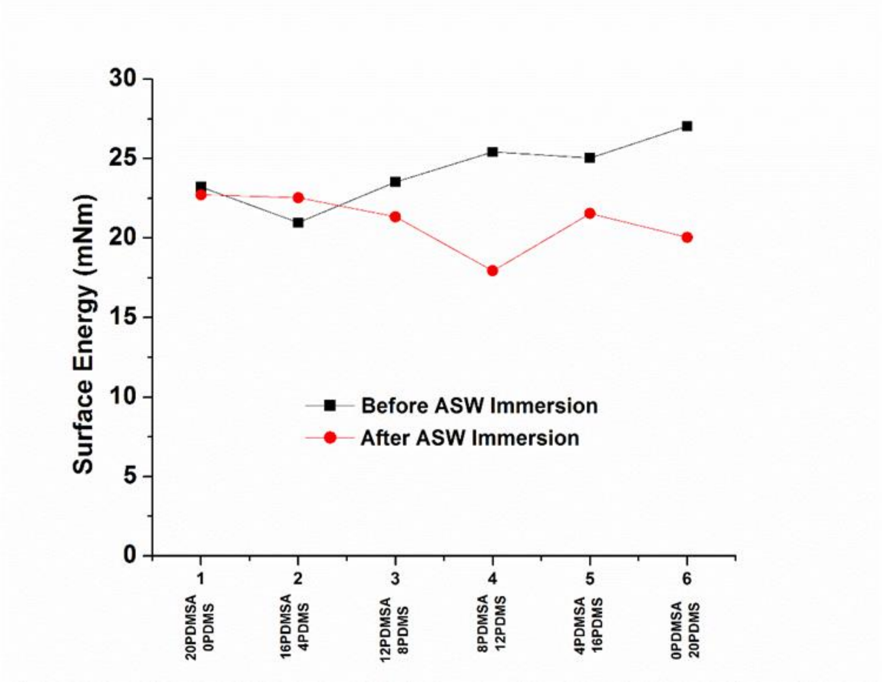
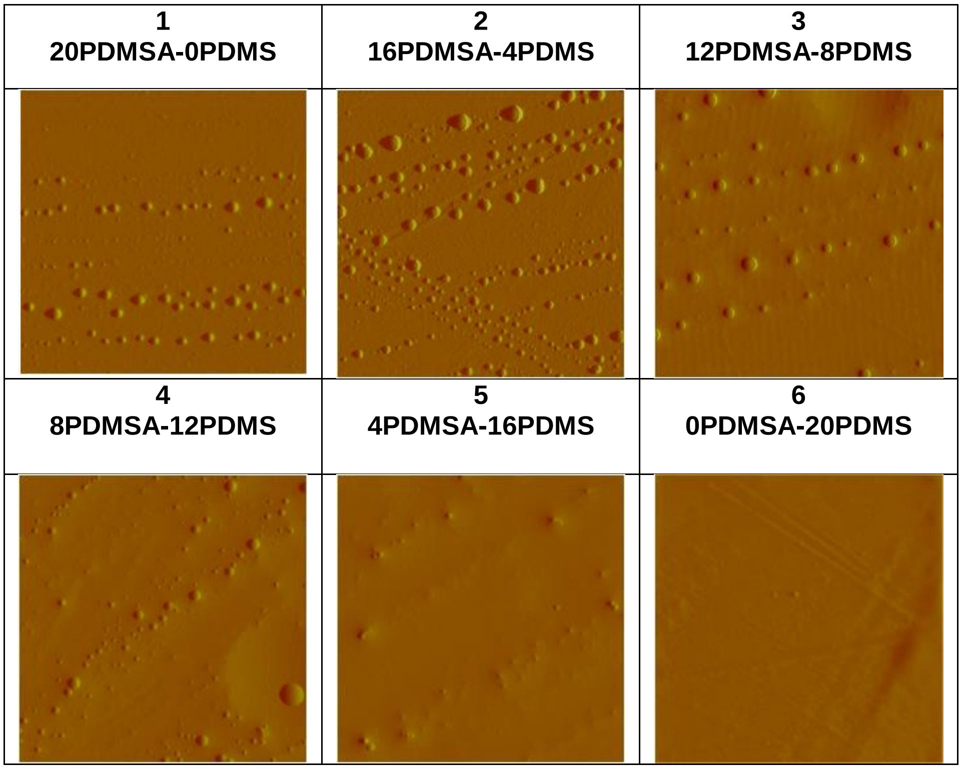


Figure 4.6. Surface energy of experimental coatings evaluated before and after ASW immersion. Each data point was calculated using the average WCA and MICA for each coating obtained from ASW water aging study

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 4.7. 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.



1
20PDMSA-0PDMS

2
16PDMSA-4PDMS

3
12PDMSA-8PDMS

4
8PDMSA-12PDMS

5
4PDMSA-16PDMS

6
0PDMSA-20PDMS

Figure 4.7. 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 4.8. 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.[46, 47] 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.[46] 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 4.9 represents 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.

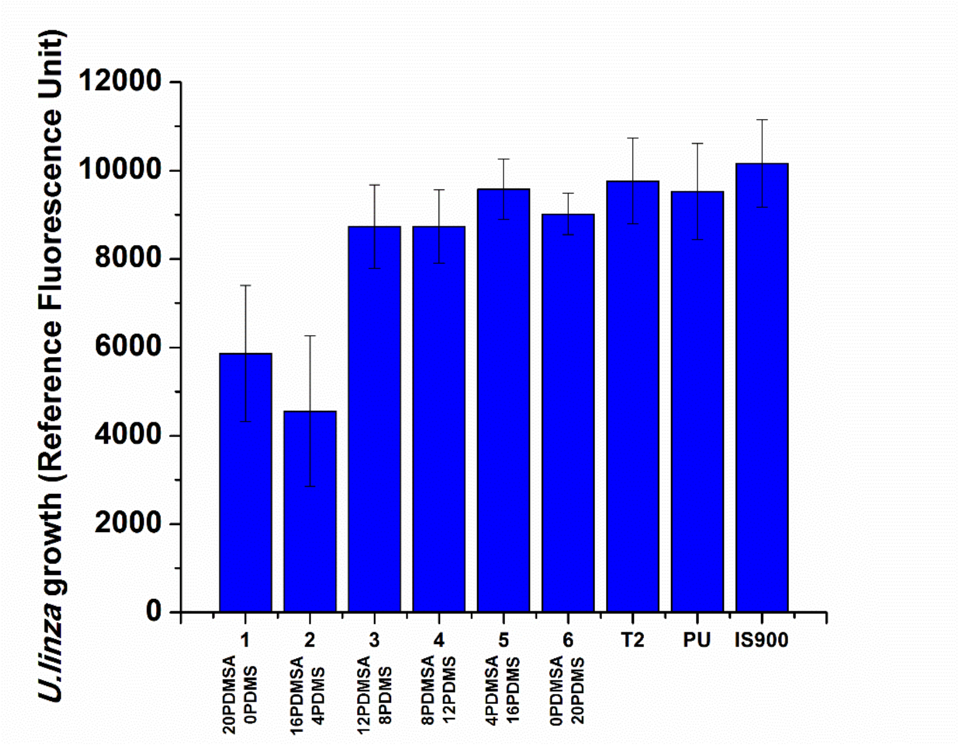


Figure 4.8. *U.linza* sporeling growth on experimental and standard coatings. Each bar represents the fluorescence of chlorophyll (averaged for 6 replicates per coating) which is directly proportional to amount of *U.linza* biomass present on the coating surface after 6 days of growth

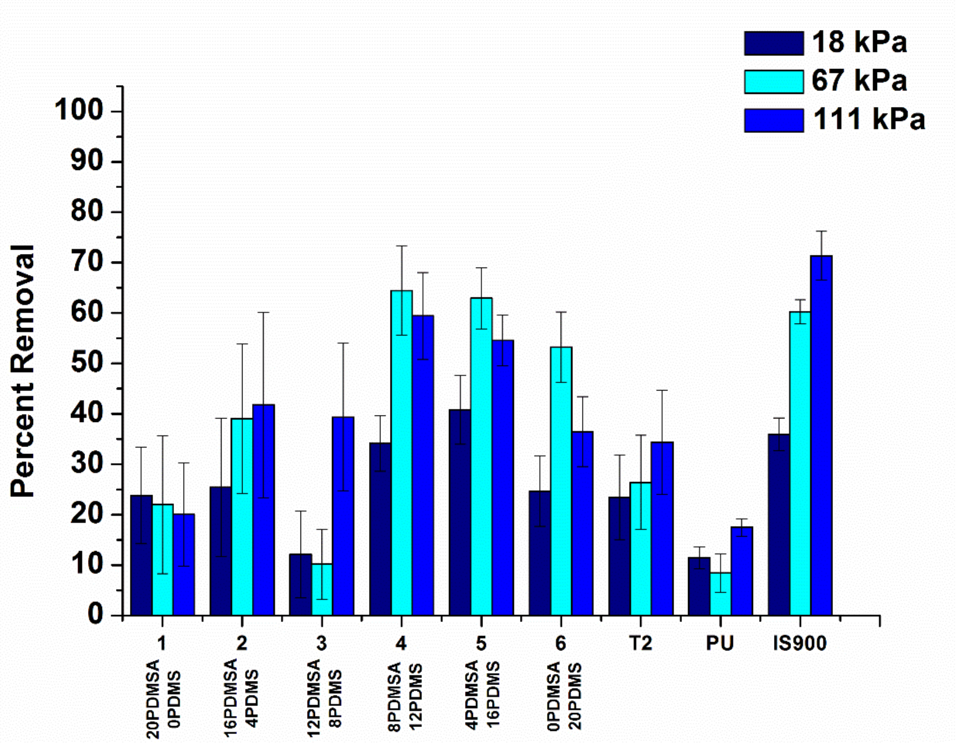


Figure 4.9. Removal of *U.linza* sporelings from coatings following water jet treatment at 18, 67, and 111 kPa. Each bar represent the average percent removal of 6 replicate measurements

Bacterial biofilm removal of the coatings indicating the FR performance of coatings towards marine bacterium *C.lytica* is shown in Figure 4.10. 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.

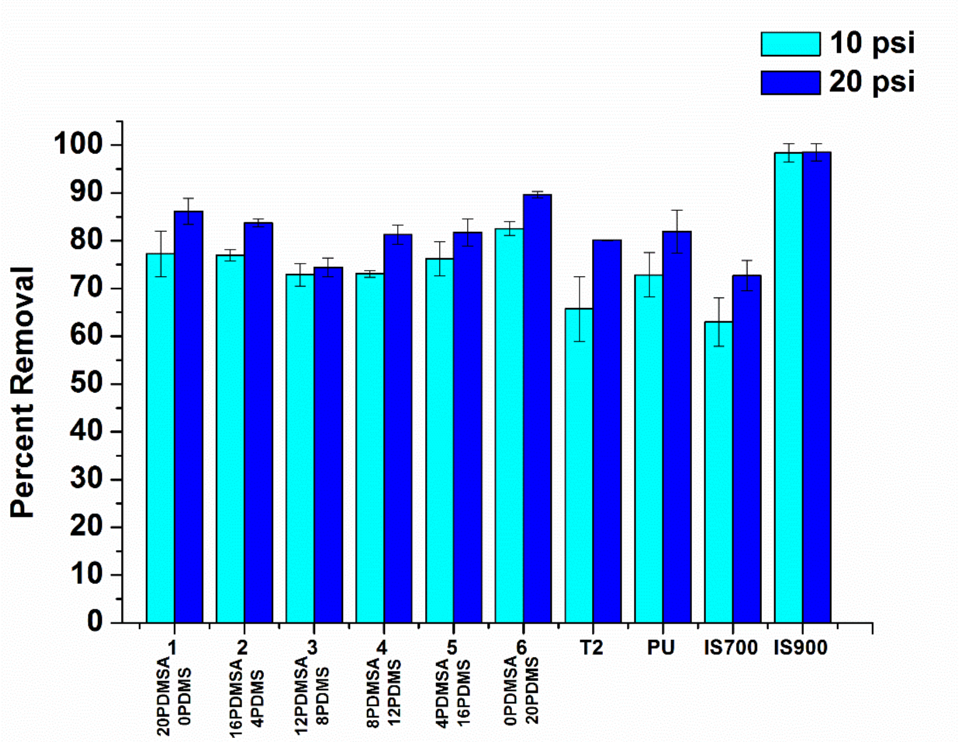


Figure 4.10. Removal of *C.lytica* bacterial biofilm form coatings following water jet treatment at 10 and 20 psi. Each bar represents the average percent removal of 3 replicate measurements

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. [47-49] 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.

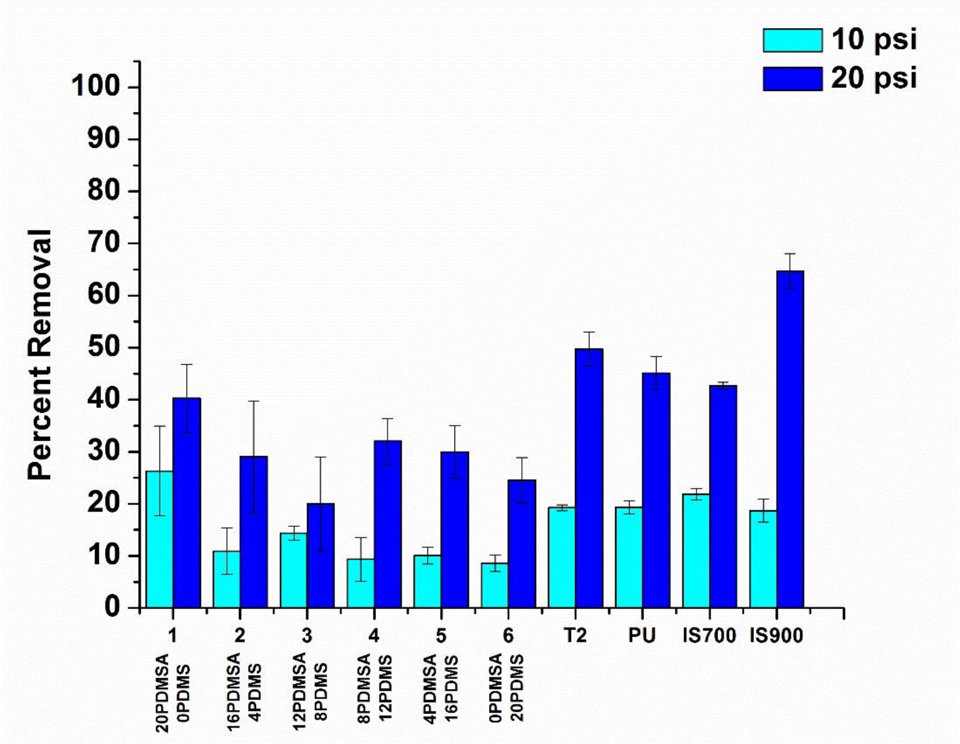


Figure 4.11. Removal of *N.incerta* microalgae from coatings after water jet treatment at 10 and 20 psi pressures. Each bar represents the average percent removal of 3 replicate measurements

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 4.12). 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.

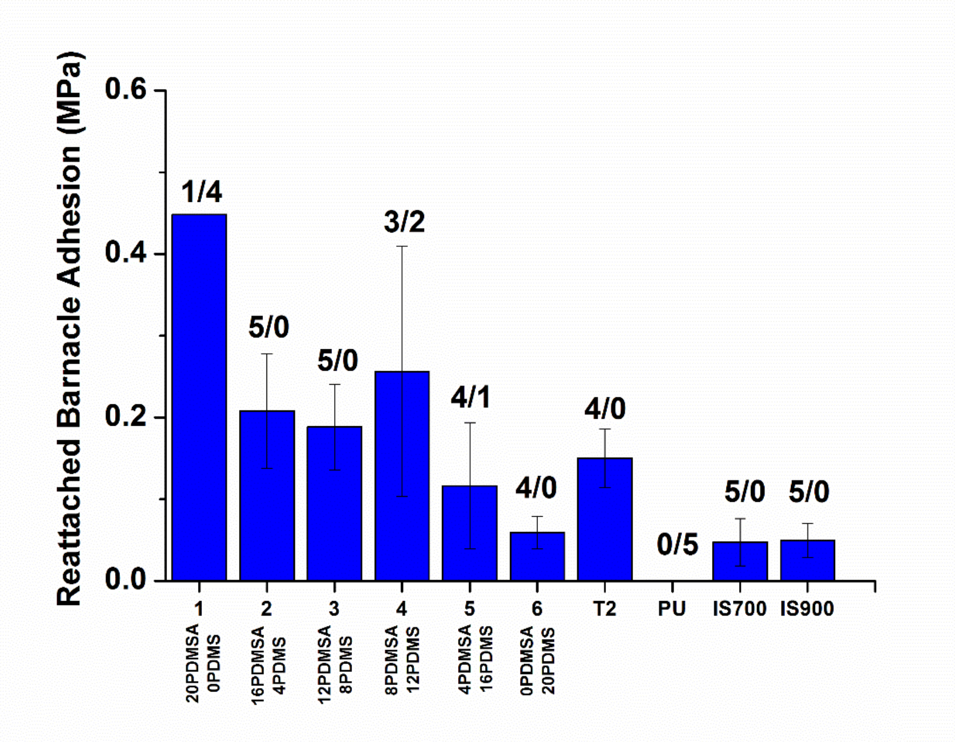


Figure 4.12. Adhesion strength of reattached barnacles (*A.amphitrite*) for coatings. Five adult barnacle reattachments were attempted for each coating. Each adhesion strength value represent the average of total number of reattached barnacles released without damage. The ratio represent the number of measured barnacles over the number of broken/damaged barnacles

Figure 4.13 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.

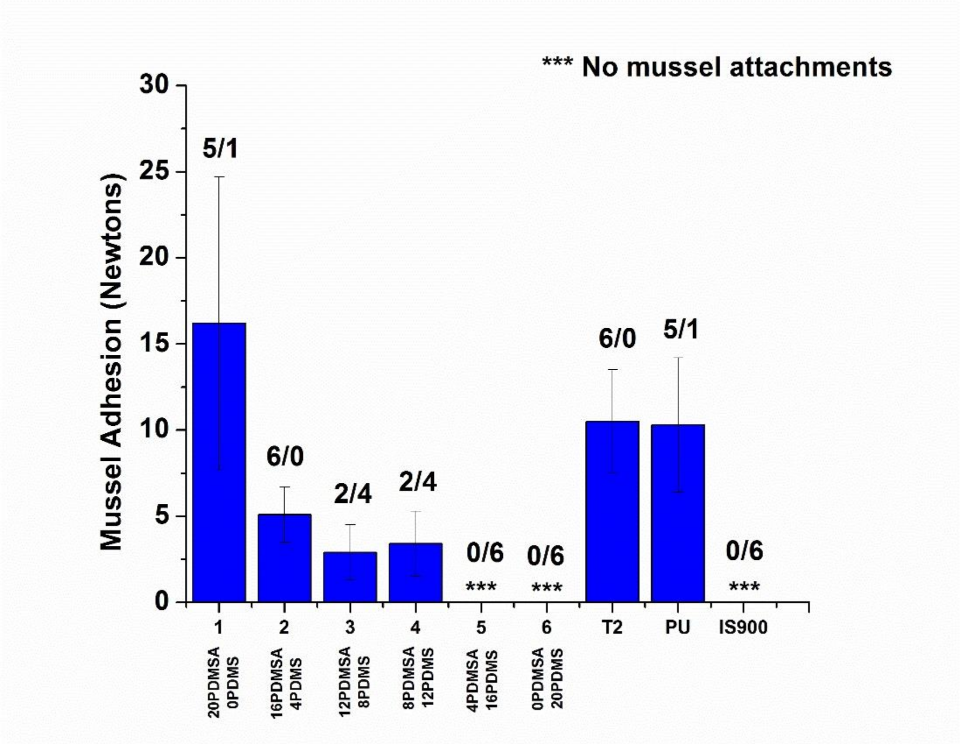


Figure 4.13. Adhesion of mussel (*G.demissa*) to coatings. Six mussel attachments were attempted for each coating. Each adhesion strength value represent the average of total number of attached mussels released from the surface. The ratio represent the number of attached mussels over the number of non-attached 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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CHAPTER 5. POLY (ETHYLENE) GLYCOL-MODIFIED, AMPHIPHILIC, SILOXANE POLYURETHANE COATINGS AND THEIR PERFORMANCE AS EFFECTIVE FOULING-RELEASE SURFACES

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.[1-3] 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.[6-8] 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.[10-12] 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.[13-15] 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. [23-28] 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 5.1). 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 Appendix Table A17.

A general structure depicted in Figure 5.1 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 Appendix Table A18. 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.

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.

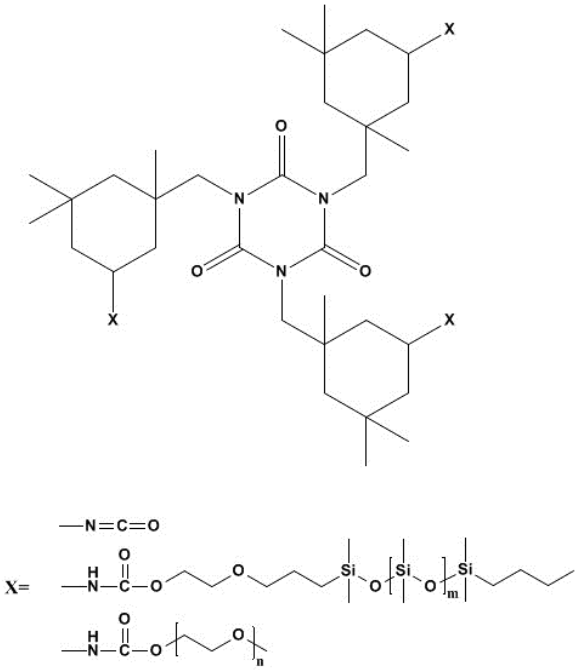

Figure 5.1. General structure of the IPDI-PDMS-PEG pre-polymers

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 5.1 summarizes the compositional details of 12 experimental coating included in this study.

Table 5.1. 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 5.2 contains detailed descriptions of the control and standard coatings used for this study.

Table 5.2. 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 Control
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) Control

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. 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 5.3 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 5.3. 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

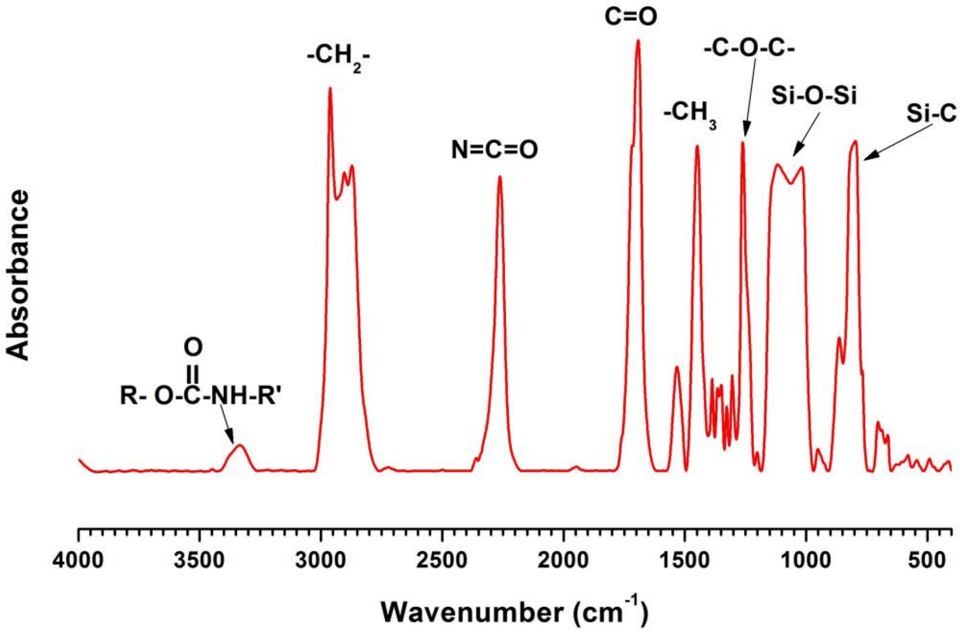

Figure 5.2. FTIR spectrum for IPDI-10-5kPDMS-550PEG pre-polymer

Figure 5.2 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 5.3 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.

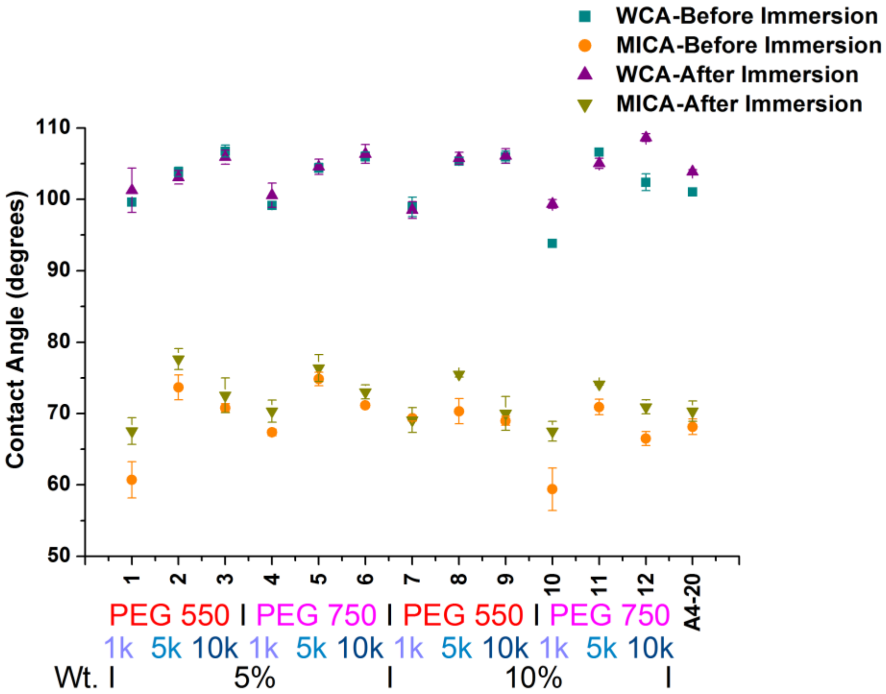

Figure 5.3. Water (WCA) and methylene iodide (MICA) contact angles for 12 experimental coatings and SiPU internal control before and after 28 days water immersion. Each data point represents the average and standard deviation of 3 measurements. X-axis is labeled to indicate the coating number, PEG MW used, PDMS MW used and wt. % of PEG and PDMS used in the coatings, respectively

Figure 5.4 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.

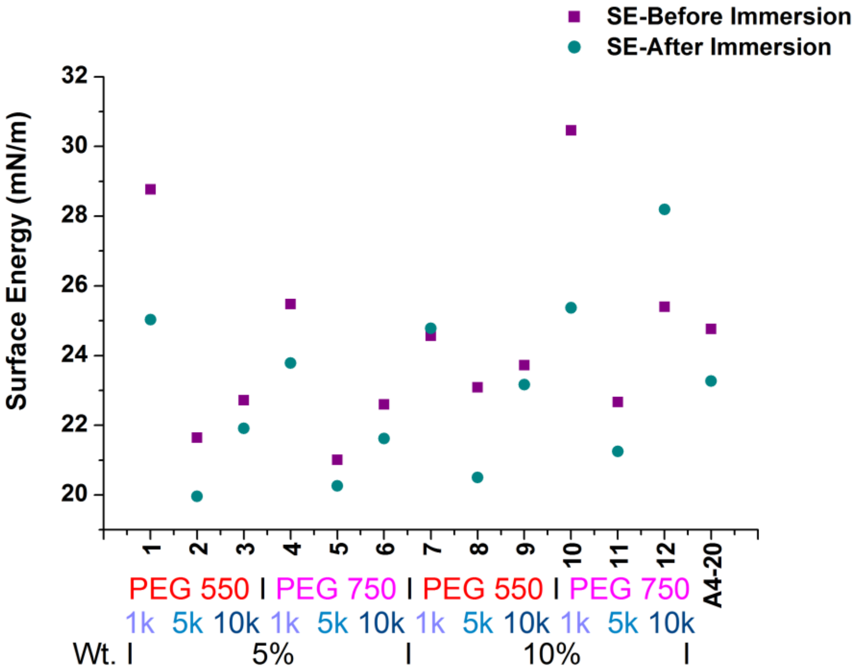

Figure 5.4. Surface energy of coatings calculated by Owens-Wendt method utilizing the average WCA and MICA measurements. X-axis is labeled to indicate the coating number, PEG MW used, PDMS MW used and wt. % of PEG and PDMS used in the coatings, respectively

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 5.5 shows the ATR-FTIR spectra for coatings 7, 8 and 9 (Table 5.1). 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.

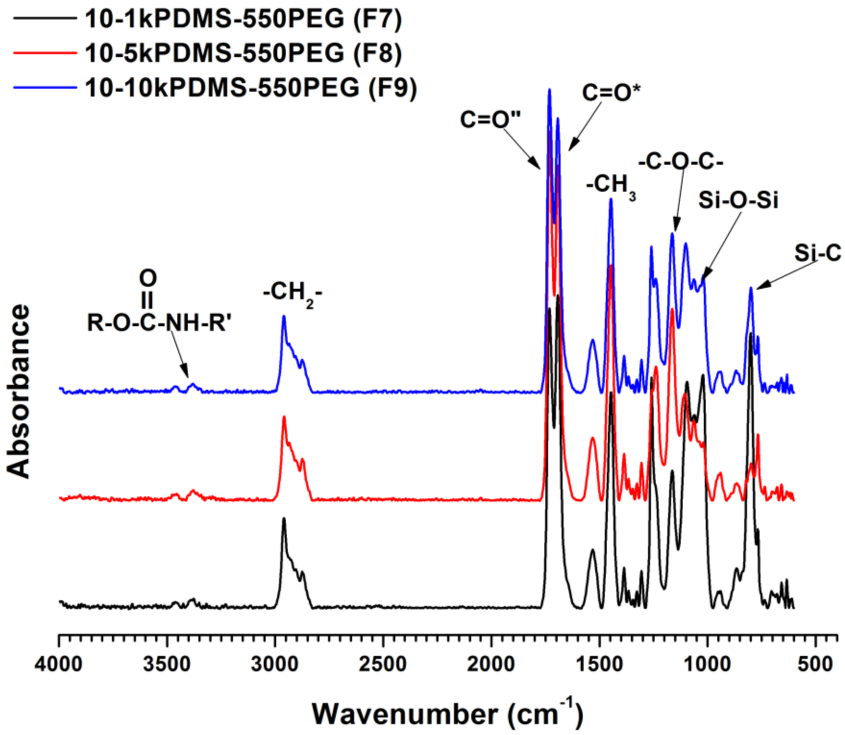

Figure 5.5. ATR-FTIR spectrum for water aged coatings (7, 8, and 9) containing pre-polymers IPDI-10-1kPDMS-550PEG, IPDI-10-5kPDMS-550PEG, IPDI-10-10kPDMS-550PEG

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 5.4 shows the estimates of atom % based on peak fitting for each coating and Figure 5.6 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). 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.

Table 5.4. 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

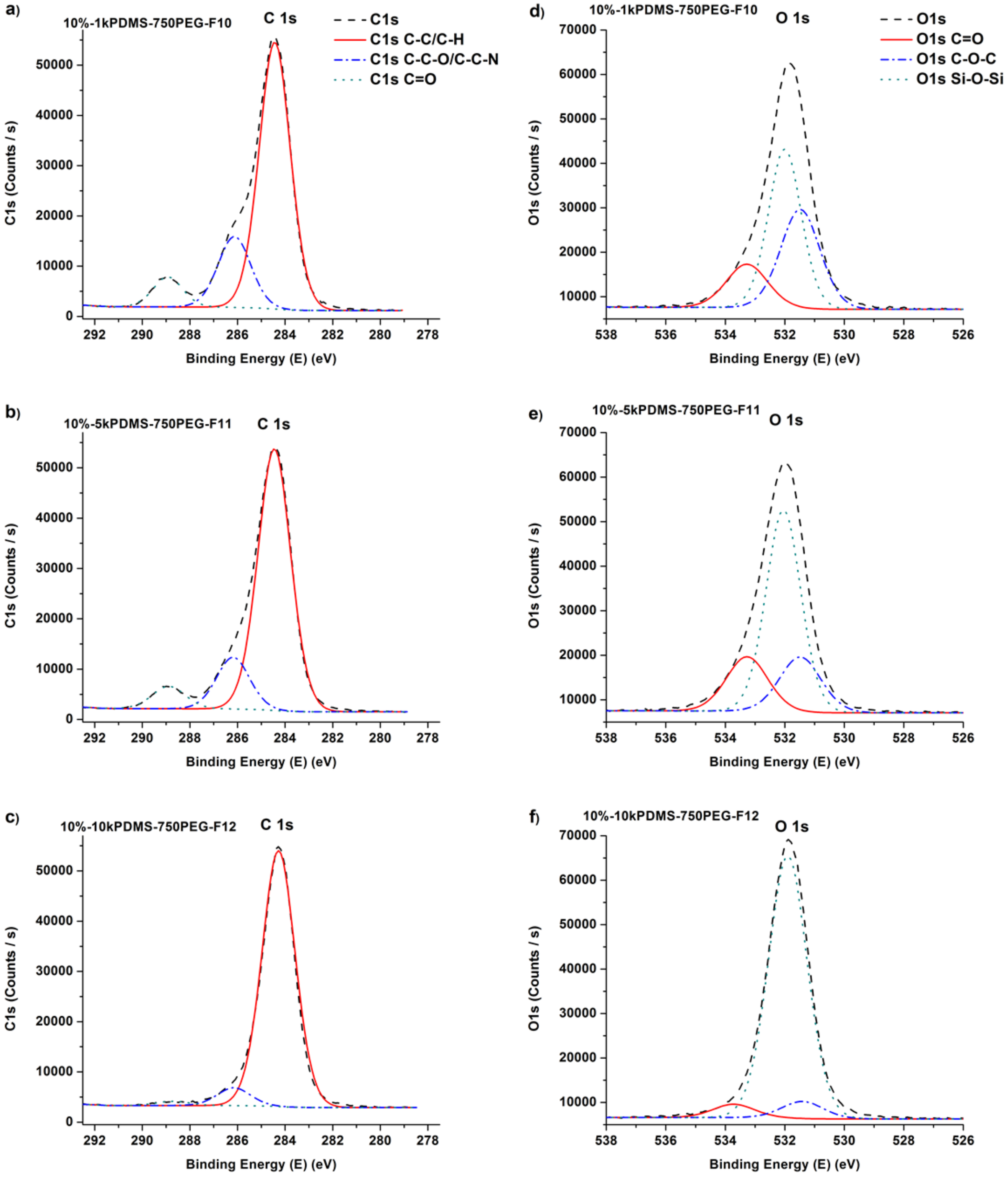

Figure 5.6. XPS spectra of AmSiPU coatings 10, 11 and 12. The plots represent C 1s and O 1s spectrum for each coating with peak fittings corresponding to chemical composition. Spectra a) and b) are for coatings 10, spectra c) and d) are for coating 11, and e) and f) are for coating 12

All AmSiPU coatings were analyzed using AFM and Figure 5.7 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.

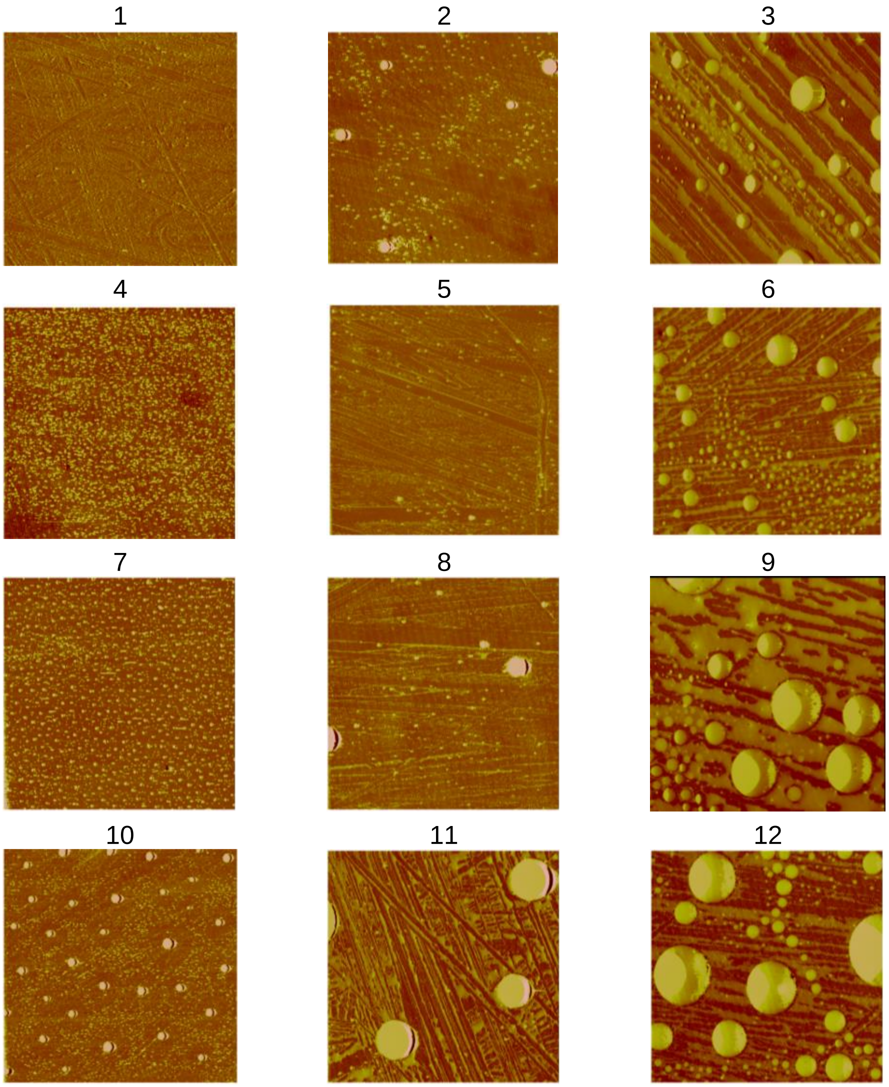

Figure 5.7. AFM phase images of AmSiPU coatings for a scan area of 100µm x 100µm

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.[43-45] 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 5.8 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.

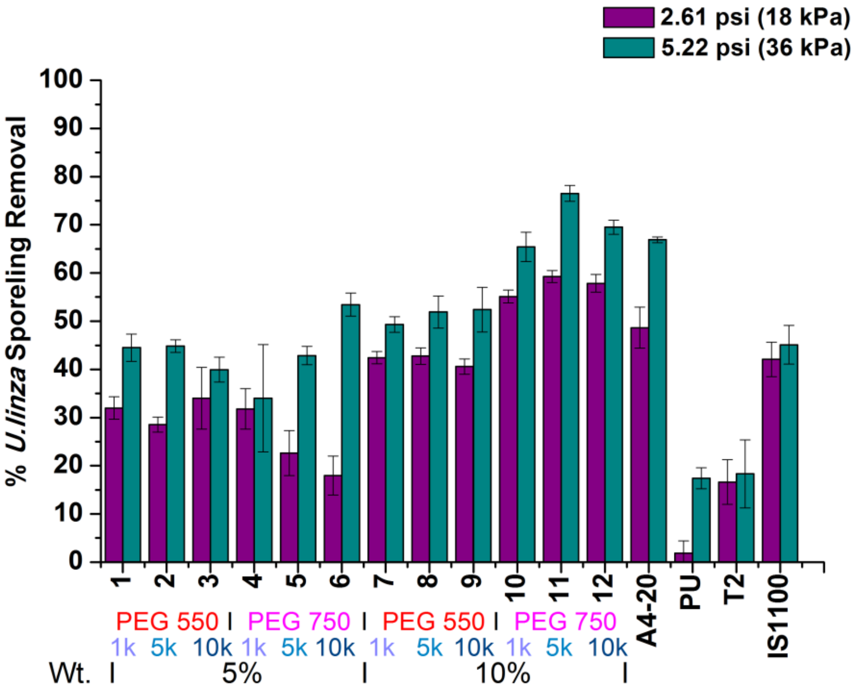

Figure 5.8. Percent removal of macroalgae (*U.linza*) sporelings at water jet treatments 18 and 36 kPa. Each bar represents the average percent removal of six measurements and corresponding standard deviation. X-axis is labeled to indicate the coating number, PEG MW used, PDMS MW used and wt. % of PEG 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.

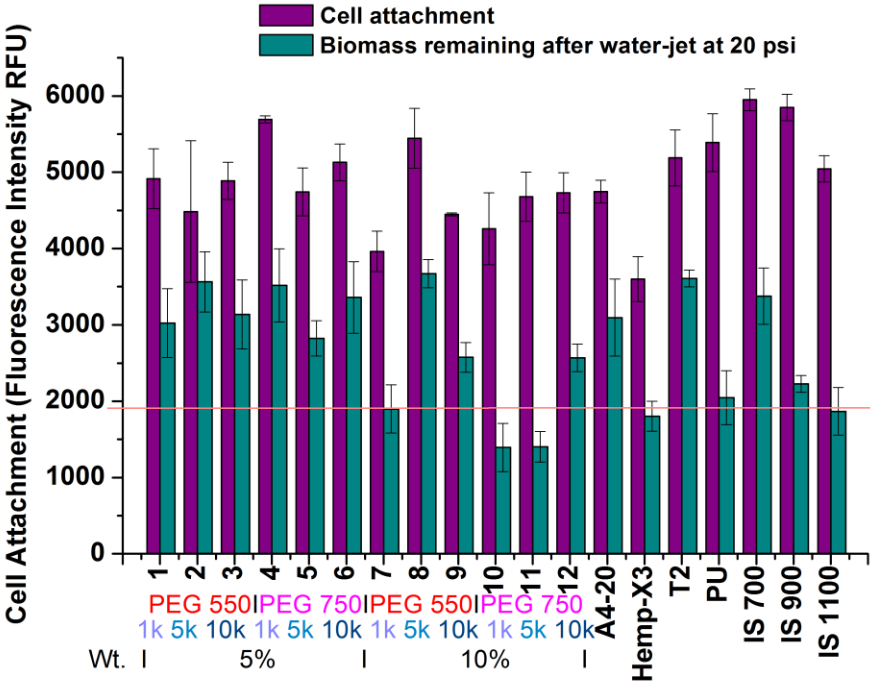

Figure 5.9. Microalgae (*N.incerta*) attachment and retention (i.e., biomass remaining) after water-jet treatment at 20 psi pressure. Each bar represents the average of 3 replicate measurements along with standard deviation. Pink colored line indicates the amount of biomass remaining on the IS 1100 commercial 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 5.11 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 5.11 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*.

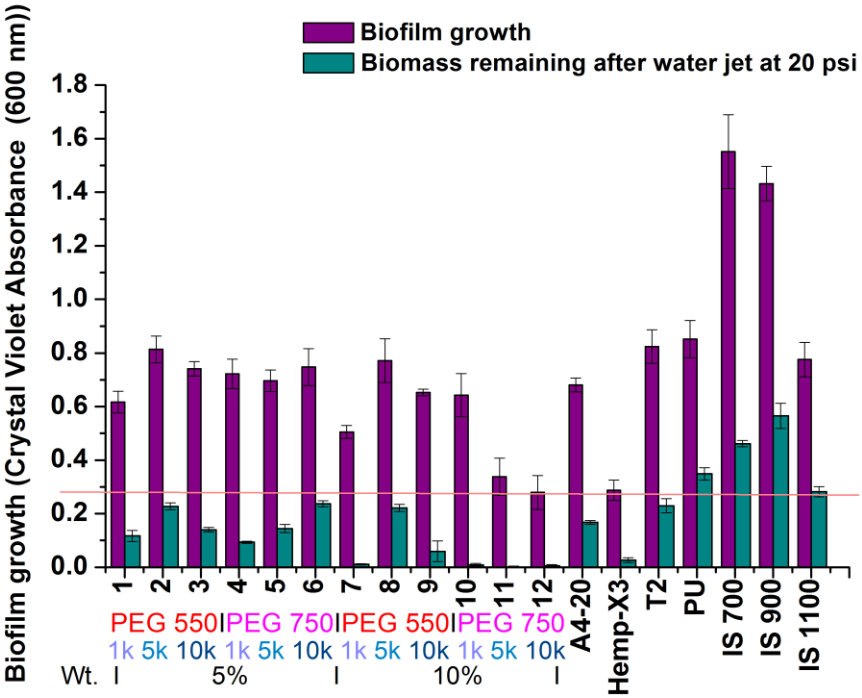

Figure 5.10. Bacterial biofilm (*C.lytica*) growth and retention after water-jet treatment at 20 psi pressure. Each bar represents the average of 3 replicate measurements along with standard deviation. Pink colored line indicates the amount of biomass remaining on the IS 1100 commercial standard after 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

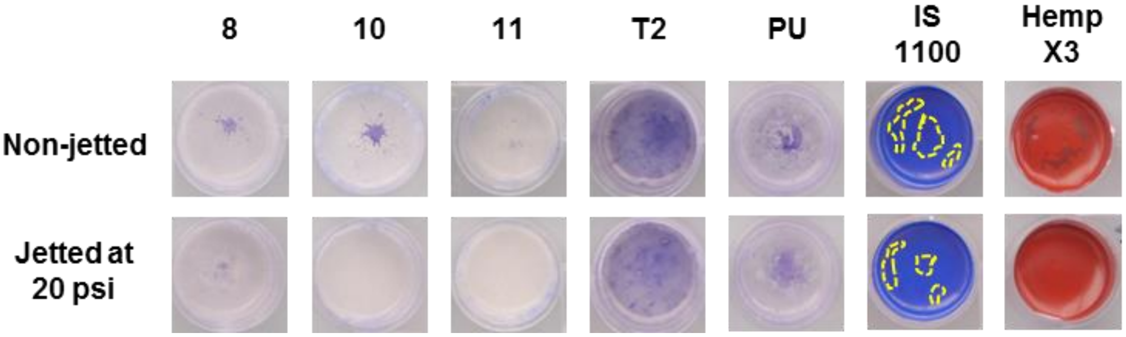

Figure 5.11. Photographs of crystal violet stained coating wells for AmSiPU coatings 8, 10, 11, standards Dow Corning® T2, polyurethane (PU), Intersleek® 1100SR and Hempasil® X3 before and after 20 psi water jet treatment. Biofilm on Intersleek® 1100SR is indicated by highlighted yellow line

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 5.12). 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.

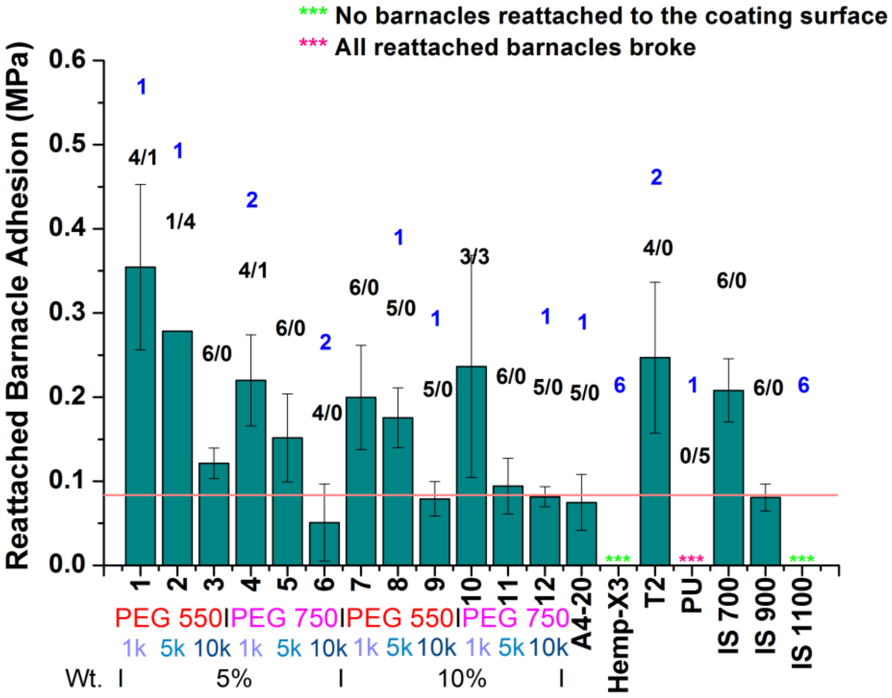

Figure 5.12. Reattached barnacle (*A. amphitrite*) adhesion strength. Six barnacles were used for each reattachment study, out of which blue numbers represent the non-attached barnacles. The ratio represents the number of released barnacles versus the number of broken/damaged barnacles during push off 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 5.13). 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.

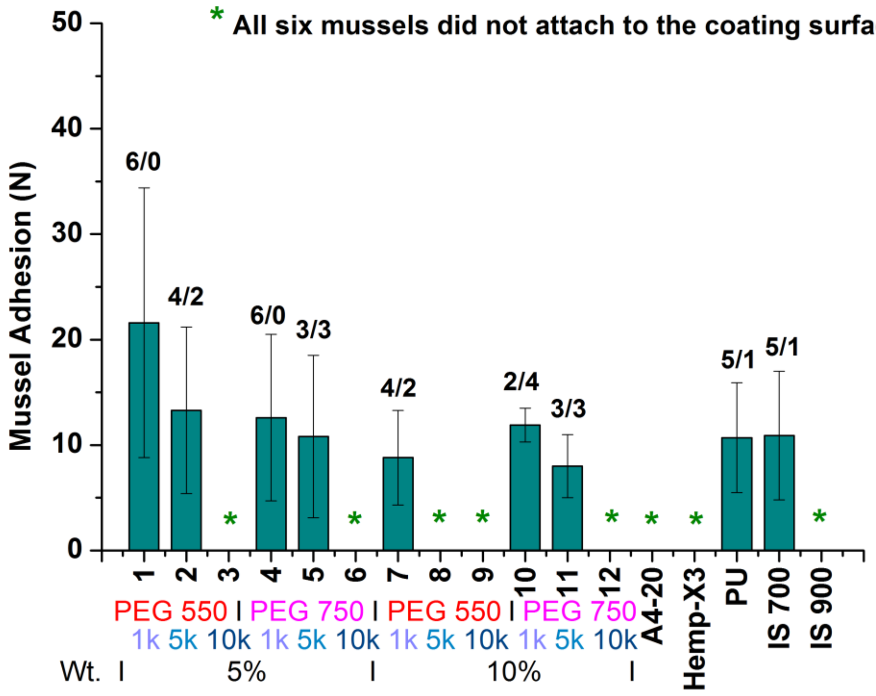

Figure 5.13. Marine mussel (*G. demissa*) adhesion evaluated with six attempted attachments for each coating. Each adhesion strength value represents the average force for removal of successfully attached mussels. The ratio represents the number of attached mussels over the number of non-attached mussels. 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.

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CHAPTER 6. 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, commercially available polyisocyanate resins were subjected to modification with hydrophilic groups such as sulfobetaine, and PEG. The modified polyisocyanates were then used to formulate SiPU coatings. 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 grafted siloxane additives were also used in small quantities in coating formulations. It was believed that these hydrophilic additives provide mobility for surface rearrangement to effectively express hydrophilic groups on the surface when in contact with water. Representative structure for the additives used in this study is shown in Figure 6.1. 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*).

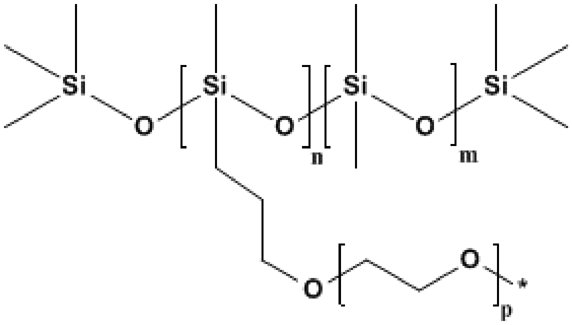

Figure 6.1. Representative structure of hydrophilic additive ethylene oxide-*graft*-dimethyl siloxane

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® 1100SR (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 6.1. 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 6.1. Pre-polymer compositions. Part1 ingredients were combined first and then part 2 ingredients were added in to part 1

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 6.2). 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 6.2. Additional bulk components added into pre-polymers from Table 6.1 to prepare SiPU coatings

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

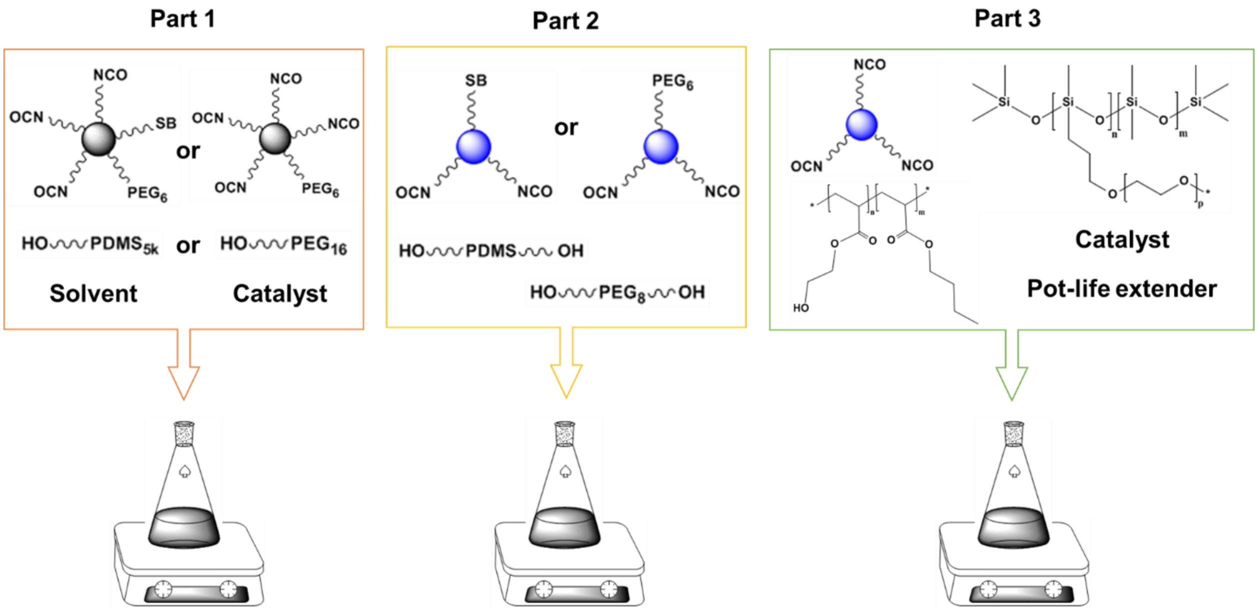

Figure 6.2. Schematic representing the coating formulation steps. In the case of coatings 9-12, part 3 was followed after part 1. The cores of polyisocyanates are color coordinated to indicate structural similarities

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 6.3 contains detailed descriptions of the control and standard coatings used for this study.

Table 6.3. 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 hrs.

Biological Laboratory Assays

Bacterial (Cellulophaga lytica) Biofilm Adhesion

Fouling-release properties towards bacteria was evaluated using retention and adhesion assays described previously.[35-37] 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.[36, 39] 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.[42-44] 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 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 6.3 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.

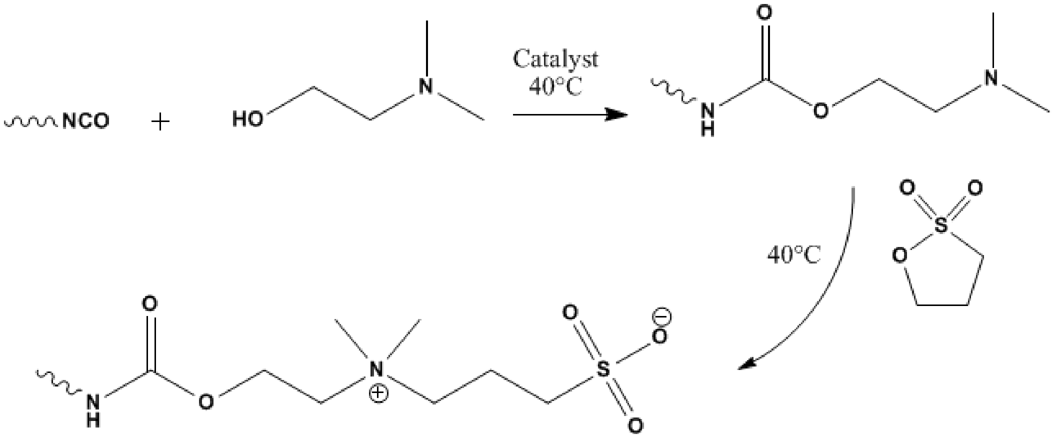

Figure 6.3. Sulfobetaine functionalization of polyisocyanates

Table 6.4 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 6.4. 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 6.4 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.

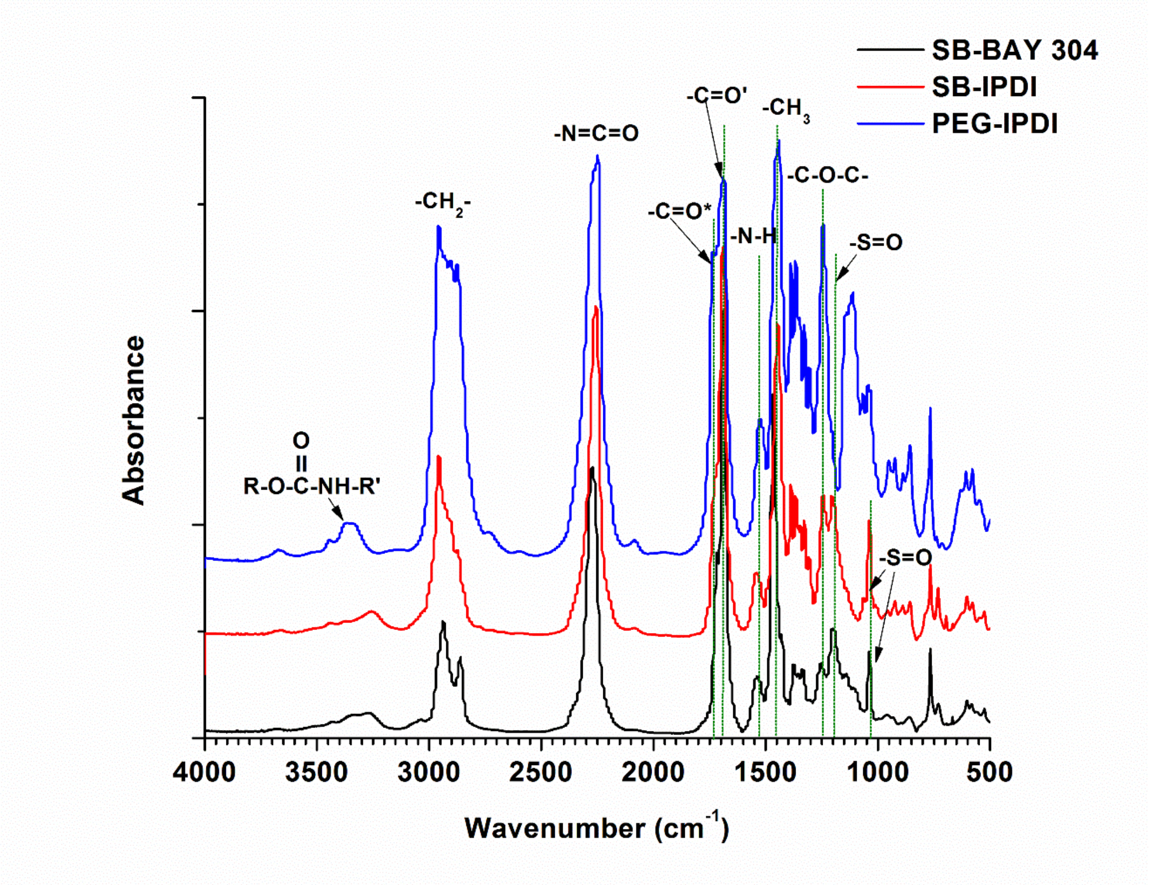

Figure 6.4. FTIR spectrum of modified polyisocyanate resins SB-BAY 304, SB-IPDI, and PEG-IPDI

Coating formulation consists of 3 distinct stages (Figure 6.2). 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 6.5 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 6.5 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 6.5 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.

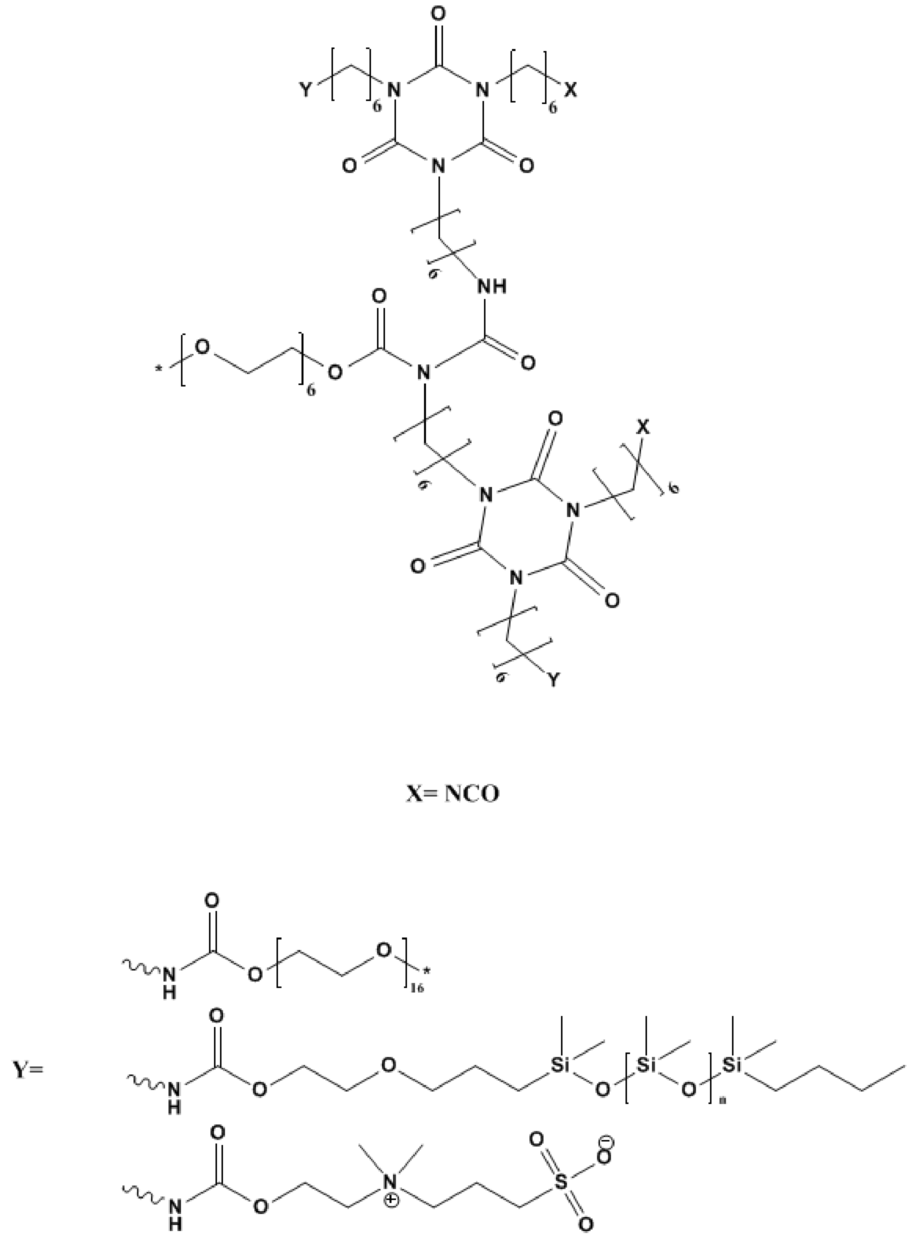

Figure 6.5. General representative structure for pre-polymers (part 1)

Figure 6.6 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 (DBE 621 and 821) vs. a single hydrophilic additive (DBE-821) 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.

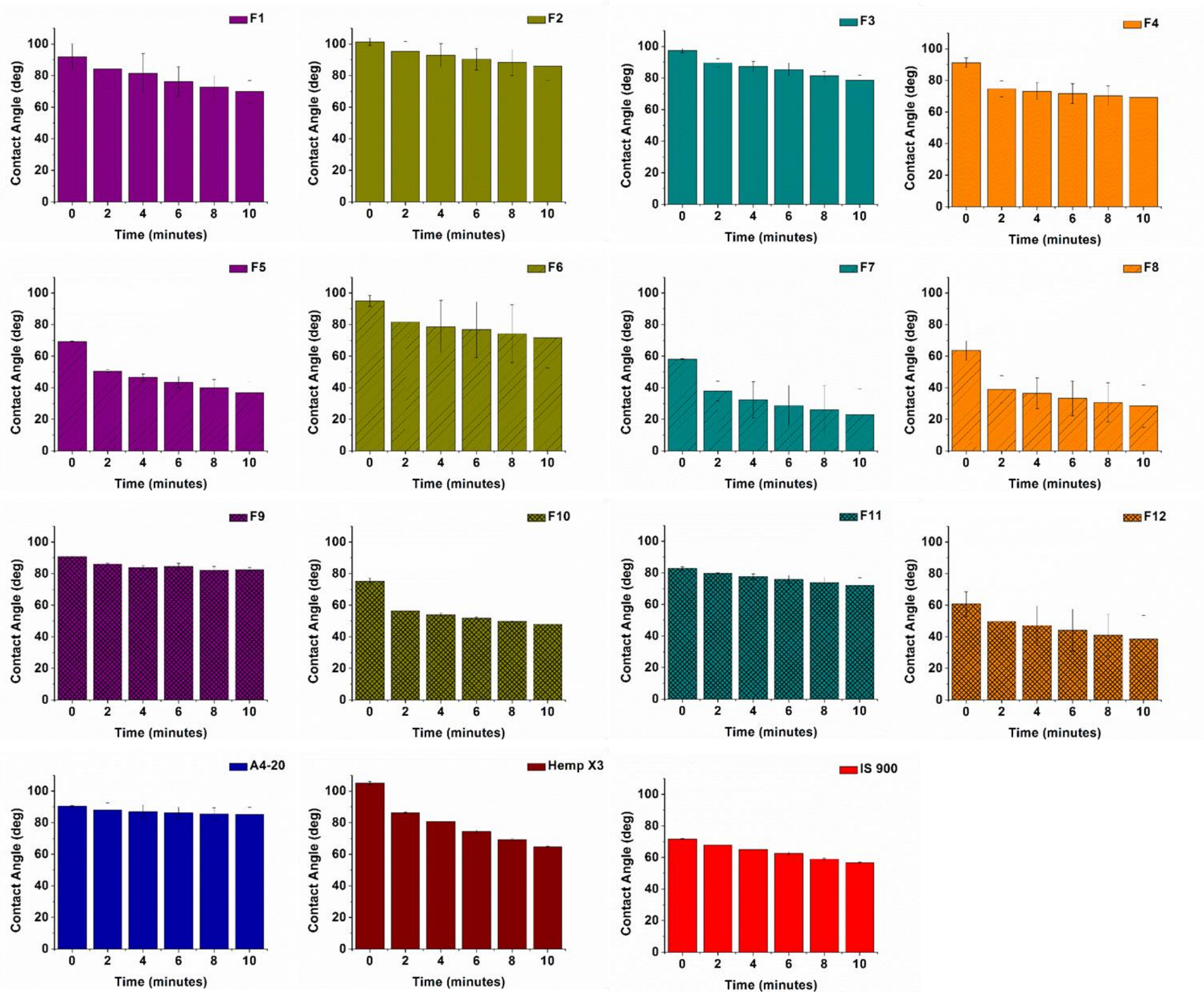

Figure 6.6. Water contact angles for coatings observed over 2 min interval for 10 min. Each bar represents the average of 3 replicate measurements and the error bars represent the standard deviation of the mean

Fouling release properties of coatings were evaluated using the *C.lytica* bacterial biofilm growth and removal assay. Figure 6.7 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 6.8 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.

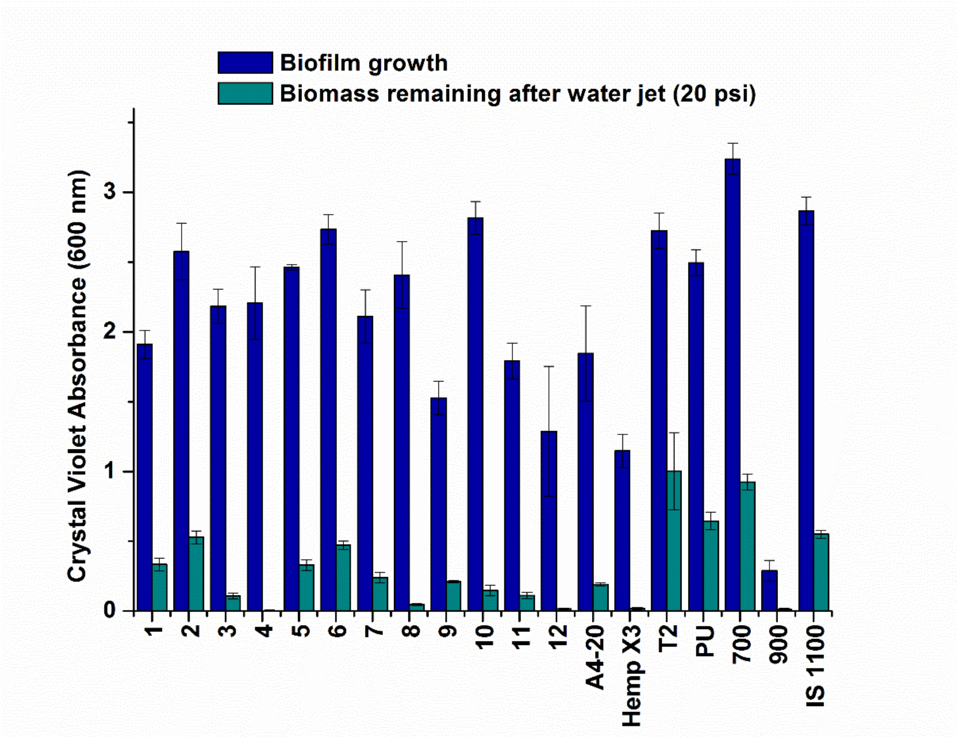

Figure 6.7. Bacterial biofilm (*C.lytica*) growth and retention after water-jet treatment at 20 psi pressure. Each bar represents the average of 3 replicate measurements and the error bars represent the standard deviation of the mean

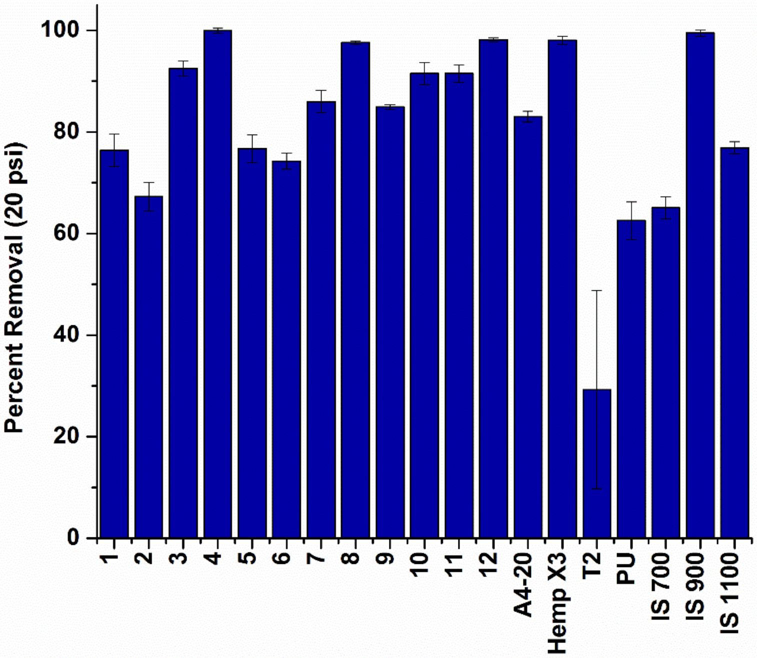

Figure 6.8. Removal of *C.lytica* biofilm from coatings. Each bar represents the average of 3 replicate measurements and the error bars represent the standard deviation of the mean

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 6.9). 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 6.10. 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.

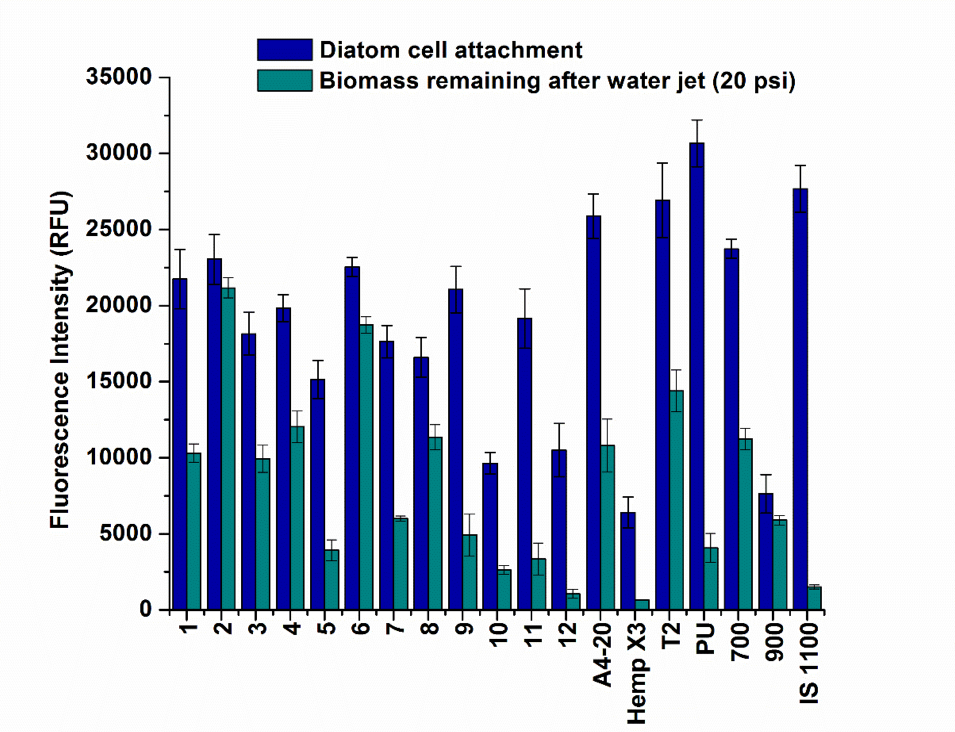

Figure 6.9. Microalgae (*N.incerta*) cell attachment and retention (i.e., biomass remaining) after water-jet treatment at 20 psi pressure. Each bar represents the average of 3 replicate measurements along with standard deviation

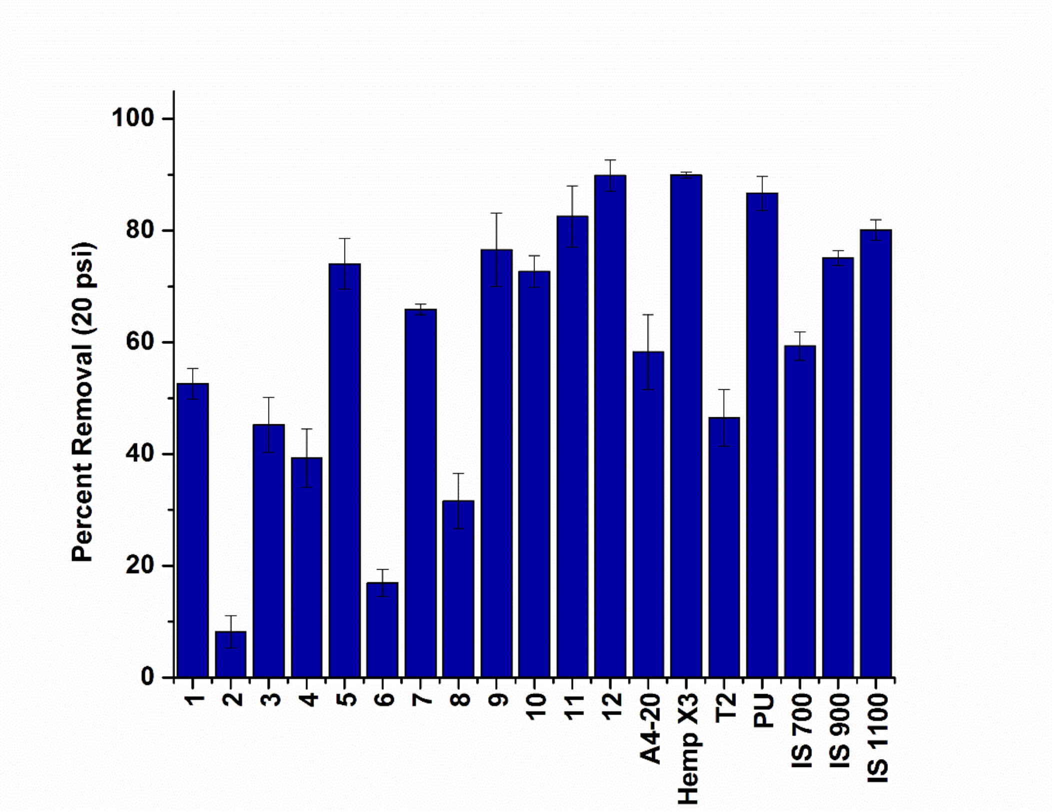

Figure 6.10. Removal of diatom (*N.incerta*) from coatings. Each bar represents the average of 3 replicate measurements and the error bars represent the standard deviation of the mean

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 6.11 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]

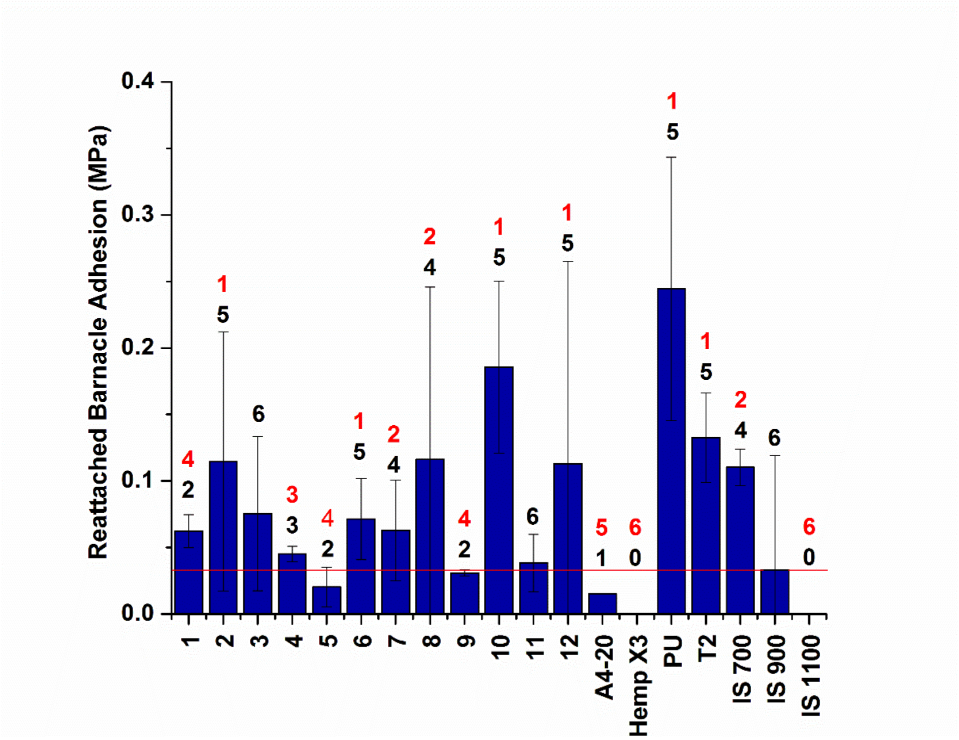

Figure 6.11. Reattached barnacle (*A. amphitrite*) adhesion strength. Six barnacles were used for each reattachment study, out of which red numbers represent the non-attached barnacles and the black numbers represent the successfully reattached barnacles. No broken/damaged barnacles were reported during 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 6.12 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.

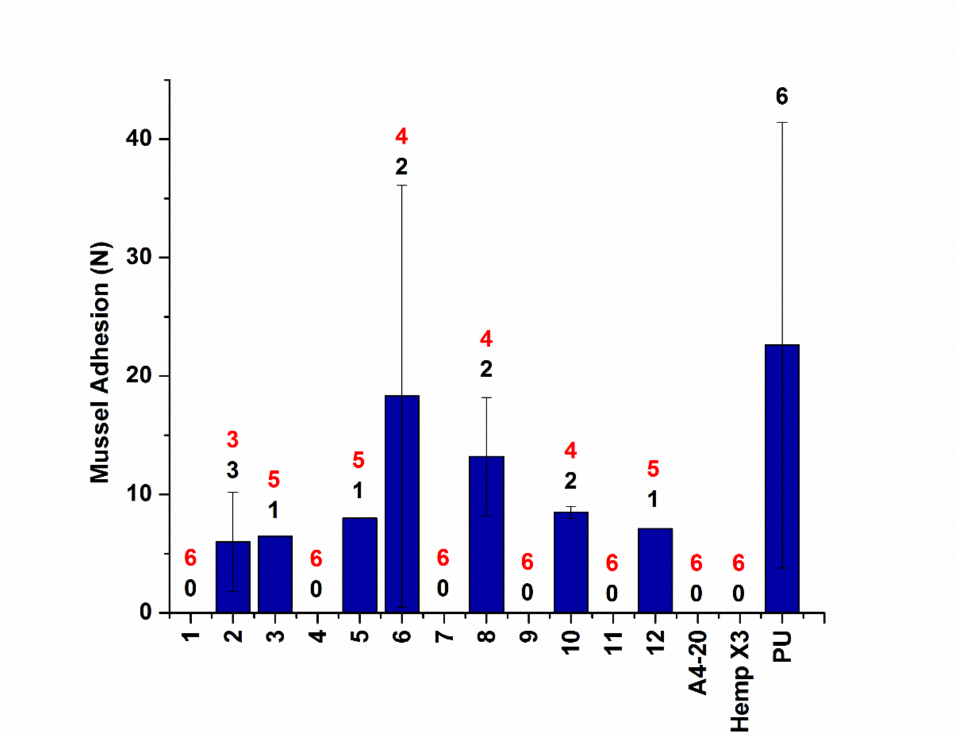

Figure 6.12. Marine mussel (*G. demissa*) adhesion evaluated with six attempted attachments for each coating. Each adhesion strength value represents the average force for removal of successfully attached mussels. Error bars represent the standard deviation of the mean. The red number indicates the number 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 (DBE-621 and 821) 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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CHAPTER 7. FOULING-RELEASE PERFORMANCE OF SILOXANE-POLYURETHANE COATINGS IN FRESHWATER FIELD IMMERSION TRIALS

Introduction

Biofouling, the buildup of aquatic animals and plants on underwater structures has caused great degree of economic impact to the seafaring vessels and the shipping industry.[1] Biofouling can negatively impact our lives in ways that we have never imagined. Unwanted accumulation of biomass on surfaces in contact with marine, human body and freshwater can significantly affect the productivity of processes involved in our daily lives. Developing practical, and environmentally friendly solution to mitigating biofouling is a modern day challenge. Even though there are many invertebrates that cause freshwater fouling, nothing can be compared to the invasion of zebra mussels which started in the Europe (around the 19th century) and more recently spread into North America.[2] Freshwater fouling has become a national concern in the United States ever since the discovery of zebra mussels (*Dreissena polymorpha*) in the great lakes (mid 1980s).[3] Zebra mussels were believed to be brought by ballast water from many cargo vessels that visited the Great Lakes from Europe.[2] This unintentional introduction of non-native species causing an imbalance in the ecosystem can be highlighted as an example for negative environmental impacts of biofouling.

Since their introduction to Great Lakes, zebra mussels have spread in to freshwater bodies and lakes in North America. In 2007, quagga mussels (Dreissena bugensis), a close cousin of zebra mussels were also spotted in Lake Mead near Hoover Dam.[3] Invasion of freshwater mussels have become a huge economic burden to hydropower plants, water purification plants, heat exchangers, and industrial complexes located in mussel infested areas costing an estimated US$500 million or more per year.[4] Considering the environmental aspects, the invasion of zebra and quagga mussels have posed concerns for balance of biodiversity in freshwater ecosystems. Studies have shown a severe decline in population density of some native freshwater bivalve species. A sudden drop of 65-100% of the Great Lakes' native bivalve population density were reported in the period from 1992 to 1999.[5] For some native species, the Introduction of mussels have led to exploitative competition for food. For others, mussel fouling (overgrowth) on their shells have led to shorten life span.[5, 6] Lately, mussels have spread down to the west affecting hydropower generation. Given the relatively warm temperatures of the water in southwest regions, mussels are being able to reproduce at faster rates compared to those in the Northern American region.[3] It is known that female mussels that have reached sexual maturity may produce 30000-40000 larvae during the reproductive season.[2] Mussels attach to surfaces by first using the byssus foot and later producing byssus threads that ends with a pad which they glue to the surface. Mussels can reposition themselves by dislodging the byssus and reattach using a new one.[2, 7] For low surface energy materials, the pad on the end of byssus thread may cover a relatively larger surface area.[7] However, given a choice they prefer not to settle on low energy surfaces.[2, 7] Also a mussel's ability to survive out of water for extended periods of time makes it difficult to control their rapid spreading through transportation of recreational boats.[4, 8]

The United States Bureau of Reclamation is the largest supplier of water and hydropower in 17 western states. They manage 476 dams, provide water to approximately 31 million people, and contribute to 17% of the hydropower generated in the United States.[3] Therefore the United States Bureau of Reclamation is responsible for managing, developing, and protecting water resources in an economical manner with the least impact on the environment in the best interest of the American public. The Bureau is facing difficulties in maintaining reservoir structures due to the uncontrollable growth of Zebra and Quagga mussels.[3] The mussels grow rapidly on structures that are submerged in water blocking water supply and transportation. In some cases attachment of mussels have completely clogged small diameter pipes and greatly reduced the flow rate of large diameter pipes. This negatively affects the efficiency of hydropower generation and created a huge economic and environmental impact. The Bureau of Reclamation has conducted a detailed study evaluating potential coating solutions for this problem. Summarizing a 3 year study they have found that fouling release coatings outperformed many other contenders during field immersion trials under both static and dynamic conditions.[3] However the silicone based fouling release coatings were eventually fouled by algae and bryozoans which may act as locations for mussel attachment.[3]

Given the service environment of the reservoir structures, the Bureau of Reclamation sought for certain requirements for coating solutions to mitigate mussel fouling. These requirements include mechanical durability, long term chemical stability, and consistent performance under highly variable water quality (sediment, debris, ice etc.). Thus siloxane-polyurethane (SiPU) fouling release coatings developed at NDSU appeared as viable candidates for fresh water fouling applications. The SiPU coatings based on the concept of self-stratification are able to combine the mechanical durability of polyurethane and the FR properties of silicone.[9, 10] Siloxane and polyurethane are incompatible with each other, once the coating is applied, siloxane self-stratifies to the surface while the polyurethane bulk provide toughness and excellent adhesion to the primed substrate. These coatings have shown similar FR properties to silicone elastomer based commercial FR coatings when evaluated through laboratory biological assays for a variety of marine organisms and in field immersion trials.[11, 12] However the FR performance of SiPU coatings have never been evaluated in freshwater environments. Therefore, select formulations from previous studies were sent to the Bureau of Reclamation upon their request for freshwater field immersion trials. Four SiPU coating compositions with slight variation in siloxane and solvent content were prepared. Panels were shipped to the Bureau in Denver and then deployed at a field test site in Parker Dam, California. Duplicate coatings were evaluated using laboratory barnacle (*Amphibalanus amphitrite*) and marine mussel (*Geukensia demissa*) assays at NDSU. Coating surfaces were characterized using contact angle, surface, and X-ray photoelectron spectroscopy (XPS) to understand the surface morphology.

Experimental

Materials

Polyisocyanate Desmodur Z 4470 BA was provided by Covestro LLC. Acetylacetone, Ethyl-3-ethoxy propionate (EEP), toluene, methyl amyl ketone (MAK) and dibutyltin diacetate (DBTDAc) were purchased from Sigma Aldrich. All reagents were used as received. A catalyst solution was prepared by diluting DBTDAc in MAK (1% by wt.). An acrylic polyol containing 80% butyl acrylate (BA) and 20% 2-hydroxyethyl acrylate (HEA) synthesized through free radical polymerization was used. The detailed synthesis of the acrylic polyol was reported previously.[13] An aminopropyl terminated poly(dimethylsiloxane) (APT-PDMS) of 20,000 g/mol molecular weight was synthesized by ring opening equilibration reaction was used as the siloxane resin. Detailed method of synthesis can be found from a previous study.[12] Intersleek® 700 (IS 700), Intersleek® 900 (IS 900), commercial FR coatings and Intergard 264 marine primer were provided by AkzoNobel International Paint. Silicone elastomer, Silastic® T2 (T2) was provided by Dow Corning (prepared coatings according to manufacturer's specifications). Aluminum panels (6 x 3 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.

Coating Formulation

Table 7.1 describes the compositions of the coatings. A general procedure for coating formulation is provided here. The non-reactive components such as, APT-PDMS (in the case of C4 formulations, APT-PDMS was diluted in 50% EEP prior to use), acrylic polyol, and pot life extender were combined in a glass container equipped with a magnetic stir bar and allowed to mix overnight. The next day, polyisocyanate and catalyst (0.05% by wt.) were added. The isocyanate to combined hydroxyl/amine equivalent ratio was maintained at 1.1:1 for all formulations. The contents were allowed to mix for about an hour. Drawdowns were made using a wire wound drawdown bar with 80µm dry film thickness on 6”×3” aluminum panels previously primed with Intergard 264 primer. Coatings for biological assays were prepared by depositing 250 µL of formulation in to multi-well plates modified with primed aluminum discs.[14] All coatings were allowed to cure for 24 hrs under ambient conditions inside a dust free cabinet, followed by force curing in the oven at 80°C for 45 minutes. A total of 6 replicate coatings were prepared for each coating formulation and 4 panels of each were sent to field immersion site.

Table 7.1. Composition of SiPU coatings.

Coatings	***APT-PDMS (wt. %)**	**Solids of APT-PDMS (%)**	**Solvent used to dilute APT-PDMS**	***Acrylic Polyol (wt. %)**	***Polyisocyanate wt. % (Desmodur Z4470 BA)**
A4-10%	10	100	-	56.80	33.20
A4-20%	20	100	-	50.20	29.80
C4-10%	10	50	EEP	56.80	33.20
C4-20%	20	50	EEP	50.20	29.80

*based on non-volatile components of the formulation

Water Aging

All the coatings prepared on both panels and plates were subjected to pre-leaching process in running tap water for 28 days. The water tanks were equipped to automatically fill and empty every 4 hours. All biological laboratory assays were carried out after the pre-leaching process was complete.

Surface Characterization of Coatings

Surface wettability of coatings were characterized through analysis of water and methylene iodide contact angles (WCA and MICA) using the Symyx® surface energy system. Three replicate measurements of each WCA and MICA were obtained using First Ten Angstroms™ software. Then, according to Owens-Wendt method, the surface energy for each coating was calculated using the average WCA and MICA values.[15] Contact angle and SE analysis were performed for as made coatings and 1 month after water immersion. Additionally, contact angle and SE measurements were performed for A4-10% and A4-20% coatings 1.42 years after withdrawal from the field test.

X-ray photoelectron spectroscopy (XPS) was utilized to investigate the morphology differences in A4-20% and C4-20% coatings. XPS experiments were conducted using the 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). Prior to conduct depth profiling of SiPU coatings, an etch rate calibration experiment was performed to determine the appropriate etch rate for silicone elastomer. 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. The coated sample was then carefully transferred to a dust free cabinet and allowed to cure under ambient conditions for 48hrs. Film thickness was determined by removing a thin strip of coating by laser ablation using the First Optec Micro Master Excimer and measuring step height from the top of the coating to the wafer substrate using a KLA-Tencor profilometer. 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 4000 eV Ar^+ source sputtering on a spot of 1 mm^2 in 30 s intervals for about 120 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 151.2 eV, and an energy increment of 0.167 eV. Silicone elastomer etch rate with Ar^+ ion etch power of 4000eV was determined to be 0.0068 nm s^{-1}. Surface morphology of SiPU coatings A4-20% and C4-20% prepared on aluminum substrates were analyzed through depth profiling experiment using same settings as above. Ar^+ sputtering was performed on a spot of 1 mm^2 of each coating with an etch power of 4000eV in 10s intervals for 25-50 min. Following each etch photoemission lines for C 1s, N 1s, O 1s, and Si 2p were collected. Atomic concentrations were determined using the integrated areas after subtracting the background. Previously determined etch rate for silicone elastomer was used to convert etch time to etch depth. Changes in coating morphology was observed by graphing atomic concentration with etch depth for each sample.

Laboratory Biological Assays

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.[16] [17] Barnacles sent from Duke University were dislodged from silicone substrates and placed on coatings (5 barnacles per coating) using a custom-designed template. The panels were then immersed in artificial seawater aquarium system and they were allowed to reattach and grow for 2 weeks 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 the ratio of peak force of removal over 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.[7] [18] [19] 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.

Freshwater Field Immersion Trials

Coatings (4 panels for each coating) were deployed at Parker Dam, California. Two panels from each coating were exposed to dynamic water flow while the other two panels were exposed to static water. For dynamic exposure, panels were tied to steel gates and placed in a depth of 40 ft. For static immersion, the panels were tied to a nylon rope and suspended 50 ft deep. The panels were first exposed in December 2012 and accumulated fouling was observed at site visits 4 months, 6 months, 1 year, 1.42 years, 2 years, 2.5 years, and 3 years after initial exposure. During each visit pictures of the panels were taken.

Results and Discussion

The invasive fouling of zebra and quagga mussels on structures under freshwater has become an economic and environmental nuisance to managing water in the United States. The spread of freshwater mussels in to south western reservoirs have led to reduced productivity of hydropower generation and water supply. The Bureau of Reclamation, the largest individual supplier of water to many southwestern states is actively seeking a robust coating solution to address these issues. SiPU coatings seemed as a good candidate for protecting reservoir statures from mussel fouling. As fouling-release performance of SiPU coatings were never evaluated in freshwater field immersion before, select coatings were sent to field testing.

The A4 and C4 formulations with slight variation in solvent content seemed to provide different levels of FR during laboratory biological assays.[12] Both A4 and C4 formulation contained 20% of APT-PDMS although for C4 formulation, APT-PDMS was diluted in EEP prior to combining with other ingredients. Contact angle measurements were carried out to evaluate the wettability of coatings. Figure 7.1 shows the WCAs for coatings. All coatings except C4-20 displayed WCA above 100° before pre-leaching. A slight increase in WCAs were observed for all coatings following water aging for a month.

After being in the field for 1.42 years, Coatings A4-10% and A4-20% maintained a hydrophobic surface having WCA above 100°. However after field immersion a slight drop in WCAs were observed for both A4-10% and A4-20% coatings when compared with the values from water aged coatings. The panels exposed to dynamic conditions had slightly lower WCAs compared to those exposed to static conditions for 1.42 years.

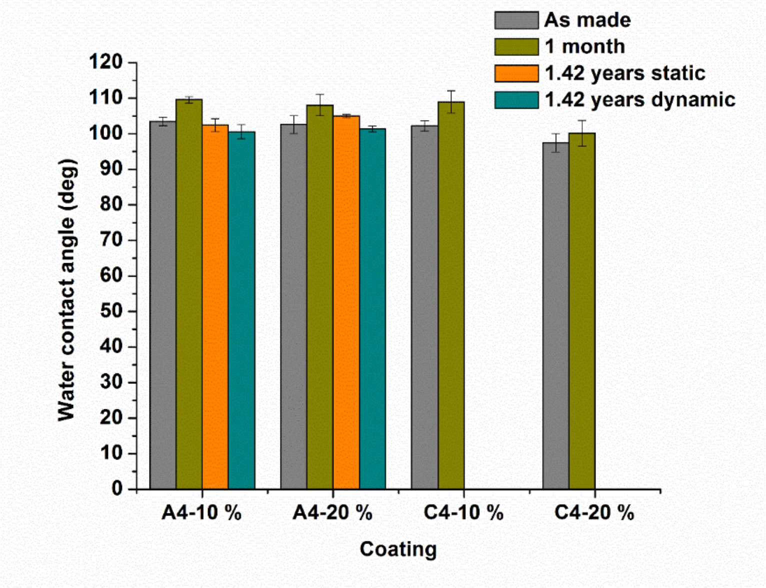

Figure 7.1. WCA for SiPU coatings under as made condition and following 1 month pre-leaching. Additionally for A4 coatings, WCAs were also performed after 1.42 years of immersion in the field test site. Each bar represent the average WCA with error bar representing standard deviation of the mean

A similar trend was observed for MICA of the coatings (Figure 7.2). Initially, all coatings had MICA in 55-63° range. After 1 month of water aging the MICAs increased to 72-78° range for all four coatings. Coating A4-10 showed a small drop in MICA after field exposure relative to that observed after 1 month water aging. Exposure to dynamic conditions slightly intensified this effect compared to static exposure. Figure 7.3 shows the observed changes in SE of coatings. Initially all SiPU coatings had SE in 25-29 mNm^{-1} range and after 1 month of water aging the SE of A4-20%, C4-10% and C4-20% dropped to ≈21-22 mNm^{-1} (close to that of PDMS). Coating A4-10% SE dropped to 18 mNm^{-1} after pre-leaching for a month. However prolonged exposure in the field under both dynamic and static conditions affected the SE of A4-10% and A4-20% coatings only slightly which was indicative of long term stability of SiPU coatings. Note that long-term results from the C4 coatings are not available since these are still under testing.

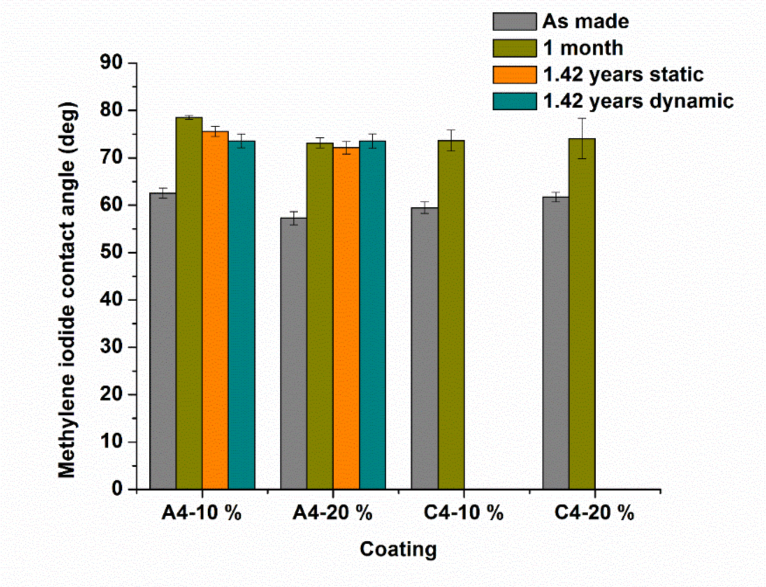

Figure 7.2. MICA for SiPU coatings under as made condition and following 1 month pre-leaching. Additionally for A4 coatings, MICAs were also performed after 1.42 years of immersion in the field test site. Each bar represent the average MICA with error bar representing standard deviation of the mean

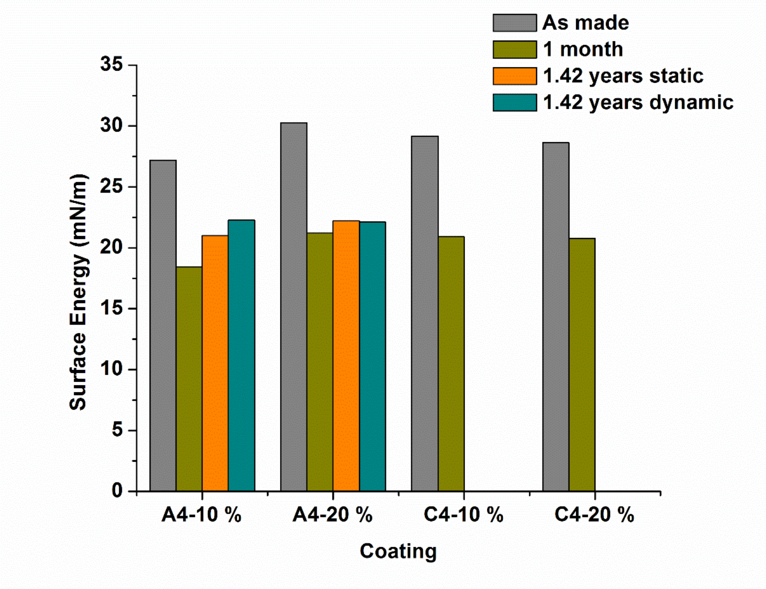

Figure 7.3. SE of coatings measured initially and after 1 month of pre-leaching. Additionally, SE measurements for A4-10% and A4-20% coatings were performed following field immersion for 1.42 years

Barnacles are one of the main macrofoulers that contributes to increased frictional drag in marine biofouling.[1, 20] The coatings prepared for field testing were also evaluated at NDSU for barnacles and marine mussels to compare with the trends from fresh water field immersion studies. Figure 7.4 shows the FR results observed for SiPU coatings and some standard coatings. All SiPU coatings demonstrated good FR since all reattached barnacles were released without damage. However the adhesion strength of barnacles to A4-10%, A4-20%, and C4-10% were relatively higher than for the Intersleek standards (IS 700 and 900) yet similar to silicone elastomer T2. Compared to all other SiPU coatings, C4-20% displayed slightly lower adhesion strength of barnacles. The adhesion strength of barnacles on C4-20% coating was very much similar to that of IS 700 but IS 900 outperformed all coatings. Pure polyurethane (PU) was a poor FR coating since all 5 reattached mussels broke during the push off test.

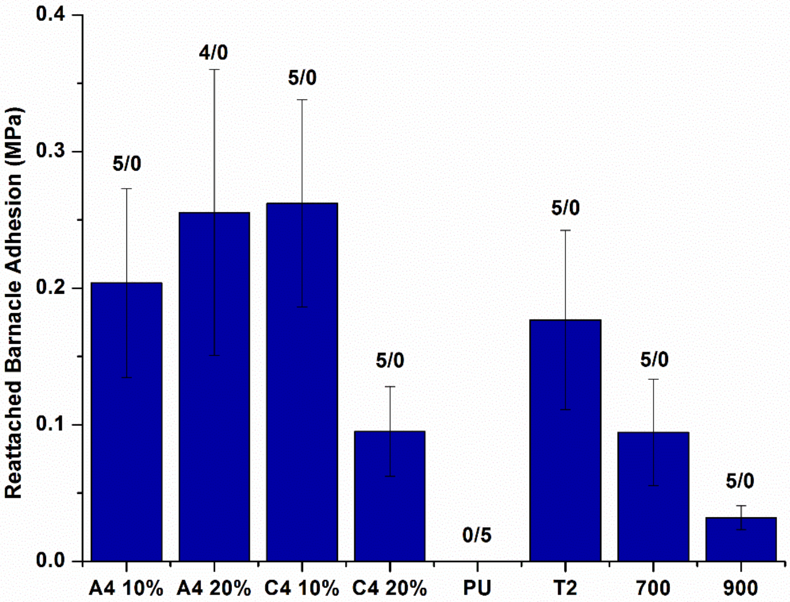

Figure 7.4. Evaluation of barnacle (A.*amphitrite*) adhesion to SiPU and stadard coatings. Each bar represents the average adhesion strength observed for succeffuly released reattached barnacles from coating surface. Error bars represent the standard deviation of average barnacle release stress. The ratio represents the number of released barnacles over the number of broken/damaged barnacles

Coatings were also tested using the recently developed 3-day marine mussel adhesion study. Figure 7.5 shows the adhesion of marine mussels on to SiPU coatings. All four SiPU coatings demonstrated excellent FR properties towards marine mussels. Fouling-release performance similar to IS 900 was observed for A4-20% coating. Coating A4-10% showed lower force for removal compared to C4-10%, although A4-10% only had 1 non-attached mussel whereas C4-10% had 3 suggesting C4-10% was better at deterring mussel settlement. Interestingly C4-20% displayed AF properties towards marine mussels by not allowing any of the 6 mussels to attach. Thus C4-20% out performed all the coatings including IS 900 commercial standard during the mussel attachment study.

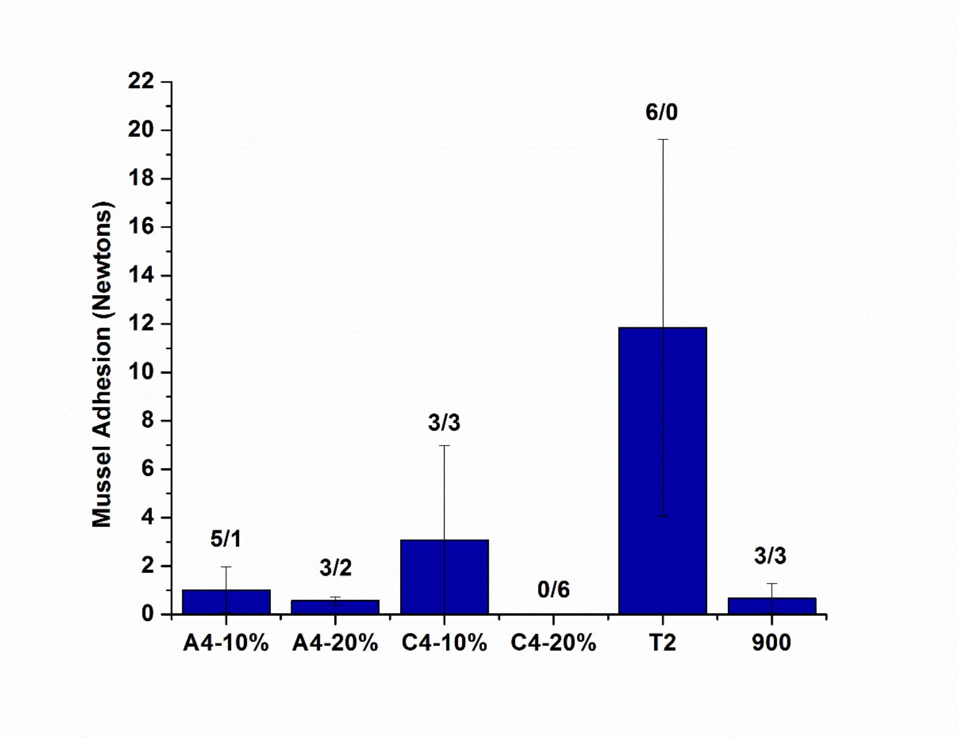

Figure 7.5. Evaluation of marine mussel (*G demissa*) adhesion to SiPU and standard coatings. Each bar represents the average force for removal of succeffuly attached mussels. The error bars represent the standard deviation of the mean adhesion force. The ratio represents the number of attached mussels over the number of non-attached mussels

Figure 7.6 shows the pictures of SiPU coating during the freshwater field exposure under dynamic conditions. Pictures were taken at 4 months, 6 months, 1 year, and 1.42 years. After 4 months of continuous immersion, none of the SiPU coatings had any mussesl attached although some slime was observed for all coatings. A4 coatings had slightly more silme fouling compared to the C4 coatings. After 6 months of dynamic immersion, still all SiPU coatings remained mussel free. However, after 1 year of immersion in fresh water, distinct differences in FR perforemce were observed for the SiPU coatings. A4 coatings were covered with mussels after 1 year of dynamic fresh water immersion while C4 coatings still remained mussel free. Specifically A4-10% had slightly more mussel fouling compared to A4-20% after 1 year exposure. It is worth noting that mussels stuggled to attach to the face of the C4-10% and C4-20% coatings as many of them attached to the zip ties and the edges of the panels. Similar results were observed after 1.42 year of continous immersion. A4 coatings were now heavely fouled with mussels while the majority of the C4 coating surfaces remained clean. Due to the decline in FR performance, the A4-10% and A4-20% coatings were removed from the field study, but C4-10% and C4-20% coatings were continued further.

Time	A4-10%	A4-20%	C4-10%	C4-20%
4 Months				
6 Months				
1 Year				
1.42 Years				

Figure 7.6. Visual appearance of SiPU coatings during freshwater field immerion trials at the Parker Dam California site exposed to dynamic conditions. Pictures were provided by courtecy of the Bureau of Reclamation

Figure 7.7 shows the pictures of C4 coatings during extended field exposure. The panels were observed and photographed after 2 years, 2.5 years and 3 years (from the initial immersion date). After 2 years of exposure, both coatings show heavy fouling of mussels around the edges of the coatings. Coating C4-10% has some mussels attached to the lower left coner of the panel. Coating C4-20% also has a few young mussels attached to the surface. Comparing the coverage, after 2 years of immersion

C4-20% coating are slightly better than C4-10% in terms of FR properties towards mussels. Observing the pictures after 2.5 years of exposure to dynamic freshwater, some fouling on the edges has fallen off (due to increased weight) but a few young mussels are attached to the surface. However attachment of these mussels tends to be aided by the presence of other fouling (mussels are mostly attached in area with a net of other fouling). After 3 years of exposure, most of the mussel have fallen off the coating surface although performance may have declined over time. Nevertheless both C4-10% and C4-20% coatings survived 3 years of field exposure demonstrating excellent FR properties towards freshwater mussels.

Time	C4-10%	C4-20%
2 Years		
2.5 Years		
3 Years		

Figure 7.7. Visual appearance of C4-10% and C4-20% coatings during continuted freshwater field immerion trials at the Parker Dam California site exposed to dynamic conditions. Pictures were provided by courtecy of the Bureau of Reclamation

Fresh water immersion trails reveled that the C4 coatings have better mussel FR properties compared to A4 coatings. These performance attributes may relate to the surface morphology of the coatings. Interestingly, the main difference between the A4 and C4 formulations is the solvent content in the formulations. Additional EEP in C4 formulations are suspected to cause some morphological differences that may explain their outstanding FR performance towards freshwater mussels. XPS experiments were carried out to understand the differences in composition and morphology of A4-20% and C4-20% SiPU coatings. The coating samples were etched using standardized silicone elastomer etch rate determined prior to depth profiling.

Figure 7.8 shows the graphs indicating the changes in atomic concentartion of C, Si, O, and N with etch depth.   For the A4 coating, surface concentration of Si and O atomic was around 30% and it quickly declined to about 5% within 3.0 nm of depth from the surface. On the other hand, surface concentration of C for A4-20% was at about 45%, which quickly increased to about 90% as Si and O concentration decreased. Although the C4-20% coating show approximately similar initial surface concentration of Si, C, and O to that of A4-20%, the C4-20% coating shows a very different distribution of elements within the coating. This observation suggests that a few angstroms past the surface, the C4-20% coating has a very different morphology compared to that of A4-20%. For C4-20% coating, Si atomic concentration showed a gradual decrease, while oxygen concentration increased up to a depth ≈ 6 nm and gradually declined. Therefore it is evident that the addition of EEP has affected the self-stratification process of SiPU coatings.

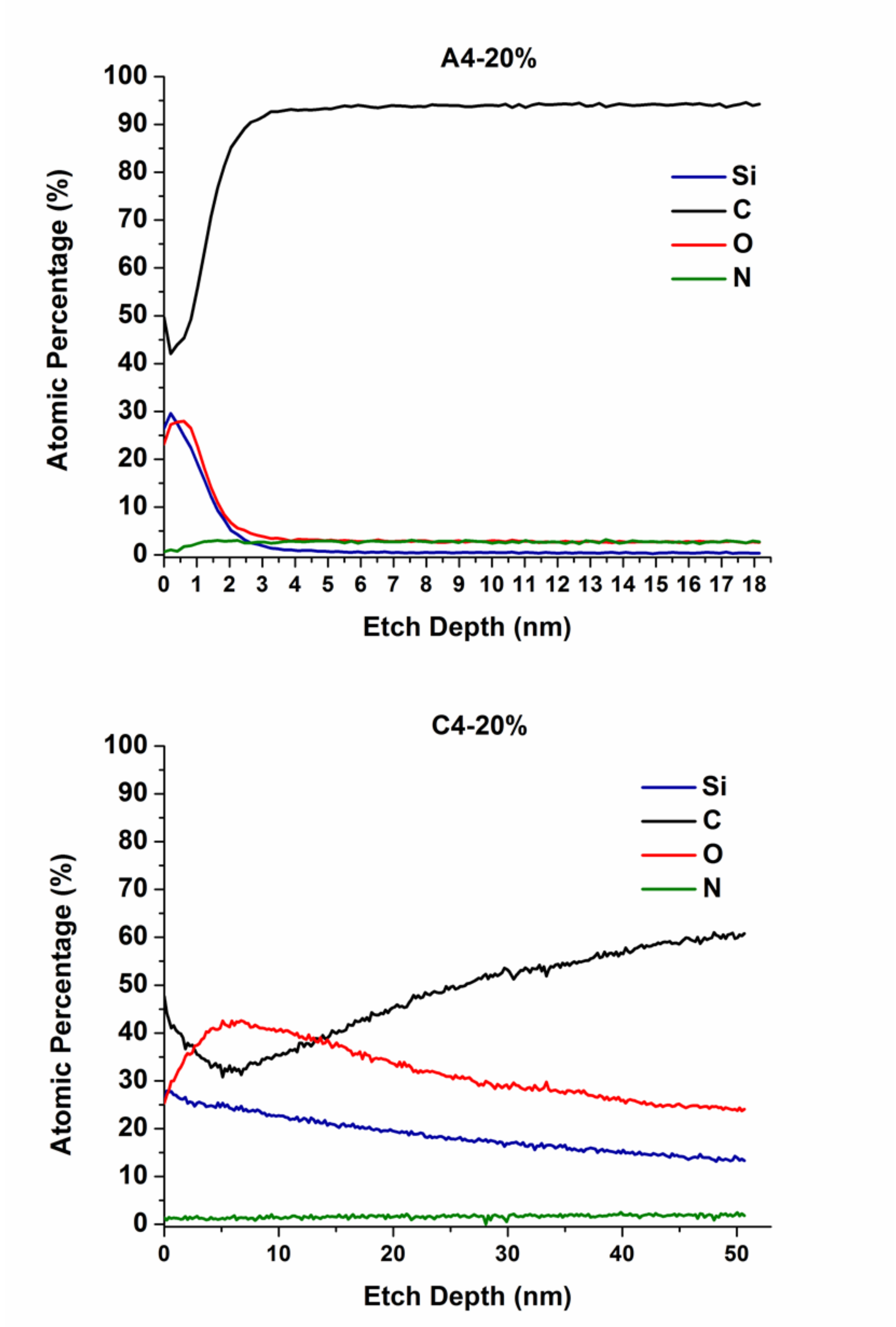

Figure 7.8. Graphs tracking atomic concentartion of C, Si, O and N during depth profiling of A4-20 and C4-20 SiPU coatings using XPS

XPS experiments reveled that having additional solvent EEP may affect the self-stratification process. Therefore understanding solvent polymer interations would provide a logical explanation to the observed morphology differences. Table 2 shows the properties of the solvents used in the SiPU coatings. Typically, a major portion of solvents used in formulations are expected to leave the coating system upon curing. However a residual amount of solvent could act as a plastizer. In fact, EEP is often used in polyurethane coatings formulations as a “tail solvent”, keeping the film open longer during the curing process. Considering the solvents present in the C4 SiPU coatings, EEP has highest boiling point, highest density, and lowest evapouration rate. Additionally EEP also has the highest hydrogen bonding interation parameter (8.8 $(J/cm^3)^{1/2}$) compared to all other solvents used in C4 coatings.[12] Thus a residual amount of EEP could potentially remain in the coating. Given the crosslinked nature of SiPU coatings, this small amount of EEP could be trapped in the coating matrix. Since EEP has a surface tension (28.5 mNm^{-1}) slightly higher than that of PDMS (22.5 mNm^{-1}), residual amounts may remain between the PDMS (top) and bulk polyurethane (bottom) layers. Previous studies on interactions of various solvents with PDMS have shown the when present in small quantities acetate functional solvents remain in a “bound state” with PDMS.[21] Therefore it is logical to hypothize that if any EEP would have remained in the coating it would remain slightly below the PDMS surface layer. Also this hypothesis may explain the anomaly in O and C atom concentration observed for C4-20% coating at around 4-10 nm during XPS depth profiling. Trapped residual EEP might have also contributed to observed superior FR of mussels in freshwater immersion trials. High water solubity of EEP (30-54 g/L) and molecular felxibity of siloxane may allow slow release of solvent lubriacting the coating water interface which could potentially contribute to improved FR properties. In a previous chapter, a similar analogy was adapted to explain the improved FR properties of phenyl-methyl silicone oil modified SiPU coatings subjected to field immersion in the ocean. However a thorough study would need to be conducted in the future to evaluate and understand the role of EEP in developing the morphology of crosslinked SiPU coatings ultimately affecting FR properties.

Table 7.2. Physical properties of solvents used in SiPU coatings

Solvent	Boiling Point (°C)	Density (g/mL)	Surface Tension (mNm^{-1})	Water Solubility (g/L of water)	Evaporation Rate (Butyl Acetate =1)	H-bonding parameter $(J/cm^3)^{1/2}$
EEP	169.7	0.951	28.1	30.0-54.1	0.12	8.8
Toluene	110.6	0.867	28.5	0.52	1.50	2.0
Butyl Acetate	126.0	0.882	25.3	6.8	1.00	6.3
2-Heptanone	151.0	0.800	24.9	4.3	0.40	4.1

Freshwater FR performance of SiPU coatings were evaluated mainly targeting to mitigate zebra and quagga mussel fouling. SiPU coatings maintained hydrophobic surface charcateristics after water immerion. Coatings showed excellent FR properties towards marine mussels (*G. demissa*) in laboratory assays. A4 coatings maintained FR proeprties towards freshwater mussels for more than 6 months while C4 coatings performed efficiently upto 2.5-3.0 years. Surface analysis of SiPU catings reveled that additional solvent EEP may affect the morphology of the coatings.

Conclusions

Select SiPU formulations were included in a freshwater field immersion study in collaboration with the United States Bureau of Reclamation. Four coatings formulations evaluated at a field test site in Parker Dam California beginning in December 2012. Results from the dynamic freshwater immersion revealed that the C4 SiPU coatings were far superior in mitigating mussel fouling in fresh water compared to the A4 SiPU coatings. Coatings C4-10% and C4-20% coatings remained mussel free up to 2-3 years while A4-10% and A4-20% declined in FR performance after a year in the field. Also C4-20% coating demonstrated the best AF properties towards marine mussels during a laboratory biological assay test and in agreement with results observed in the fresh water field testing. Surface analysis experiments were conducted using XPS to understand the variations in coating morphology to possibly explain the observed FR performance differences. A4-20% and C4-20 coatings had different morphologies which may be attributed to additional solvent EEP used to formulate C4 coatings. Also, contact angle and SE measurements suggested that SiPU coatings maintain a fairly hydrophobic surface even after prolonged exposure in the field. On another note, all SiPU coatings maintained their mechanical integrity throughout field testing which make them viable candidates for durable FR applications. This study also opened up a new area of application for SiPU coatings.

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CHAPTER 8. OVERALL CONCLUSIONS AND FUTURE WORK

Several approaches were explored to optimize the surface properties of siloxane-polyurethane (SiPU) coatings with the intention to improve fouling-release (FR) performance. Non-reactive phenyl-methyl silicone oils were used as an additive in SiPU coatings and the effects on FR properties were studied in relation to characteristics of the oils. SiPU coatings were formulated incorporating wide variety of phenyl-methyl silicone oils into the optimum SiPU formulation which was identified from previous studies (A4-20) and evaluated for their FR performance through a series of laboratory biological assays. Improvement in FR properties was observed for green algae, barnacles and mussels due to the incorporation of nonreactive silicone oils. Several phenyl-methyl silicone oil modified coatings showed efficient *Ulva linza* sporeling removal (at light water jet pressures), comparable to commercial standards. Low adhesion strength of reattached barnacles (*Amphibalanus amphitrite*) was observed for SiPU coatings with phenyl-methyl homopolymer oils. Regardless of the phenyl-methyl composition, good anti-fouling (AF) properties towards marine mussels (*G. demissa*) were observed for SiPU coatings modified with 500 cs viscosity silicone oils. Improvements in FR properties were consistent with the results observed for select silicone oil modified coatings in field immersion trials. SiPU coatings modified with phenyl-methyl silicone oils showed better FR properties than A4-20 and comparable performance to Intersleek 900 standard during prolonged field exposure in natural marine environment. Surface analysis using X-ray photoelectron spectroscopy revealed that silicone oil self-stratified with PDMS and remained close to the surface. Therefore, it was proposed that silicone oil may exude over time, providing interfacial slippage which may have led to improved FR properties both in laboratory assays for model organisms and in seawater field immersion trials.

Improving surface lubricity seems to help in minimizing the adhesion strength of marine organisms. However FR properties may eventually decline when lubricating oil is depleted. Therefore, methods to replenish or control the release of lubricating oil would be beneficial for long term FR performance. However, a way to effectively incorporate and release lubricant fluid in a controlled manner can be challenging. Encapsulating lubricant fluids like silicone oil and incorporating them into the coating matrix can be pursued as a potential way to improve FR performance of SiPU coatings. There are many studies that discuss methods to encapsulate silicone oil, one of the more frequent methods mentioned is through emulsion polymerization. Silicone oil incorporated gels are widely discussed for applications in the cosmetics industry which may be modified and adapted to prepare SiPU coatings with oil encapsulated gels.

Since phenyl-methyl silicone oils provided improved FR properties, the effect of phenyl functionality on FR properties of crosslinked SiPU coating system was investigated. Aminopropyl terminated polydiphenyldimethyl siloxane (APT-PDPDMS) copolymer was synthesized and blended with APT-PDMS at different weight ratios to study the effect of phenyl content on FR properties of SiPU coatings. Phenyl modified SiPU coatings displayed micro-scale surface features in regard to compositional variations when characterized using Atomic Force Microscopy (AFM). The FR properties of these coatings were strongly affected by the presence of surface features. Microfouling organisms demonstrated weak FR properties while macrofouling organisms seemed to show good AF/FR properties. Marine mussels were unable to attach to any of the phenyl modified SiPU coatings during the 3 day attachment period and several coating compositions showed non-attached barnacles. While a coating with spike-like surface features did not allow adhesion of barnacles, a few experienced high adhesion strength of barnacles. The results observed for FR properties of phenyl modified coatings towards model organisms may be explained using the attachment point theory. Since the size scale of the surface features observed for phenyl modified coatings were relatively larger than that of microfoulers, organisms adhered strongly finding refuge settling between the gaps of the features.

In previous studies, amphiphilic acid functional PDMS showed excellent FR properties towards diatoms while that of barnacles were impaired. In order to address the short comings, 25% acid functionalized aminopropyl terminated PDMS (APT-PDMS-25A) was blended with APT-PDMS to prepare SiPU coatings. It was hypothesized that tuning the hydrophilic acid groups on the surface may result in improved FR properties towards barnacles while maintaining diatom FR properties. In fact, water contact angle measurements indicated that the wettability of SiPU surface went from being hydrophobic to hydrophilic with increasing concentration of APT-PDMS-25A copolymer in the coating composition. Interestingly, the FR performance of APT-PDMS-25A modified coatings showed improvement towards barnacles yet diatom removal was significantly affected. The coating compositions with high APT-PDMS-25A concentration also showed low settlement of *U.linza* although sporelings adhered strongly to those coatings. Obtaining FR properties to a broad range of marine organisms seems to be quite challenging using acid functional PDMS. Also, some marine organisms secrete proteins that may be more accretive to surfaces with surface net charge (in the case of acid modified surfaces COO^- groups). Therefore alternate hydrophilic functionality should be used for further exploration.

An amphiphilic approach to mitigate biofouling using polyethylene glycol (PEG) was also explored previously. In an earlier study, siloxane polymer with PEG side chains was used to prepare SiPU coatings. Although the synthesis of PEG modified siloxane resin included multiple steps, some improvements in FR properties were observed. Therefore, a more straight forward method to obtain amphiphilic siloxane-polyurethane (AmSiPU) coatings was attempted. In a recent study, polyisocyanate pre-polymers modified with monofunctional PDMS and PEG were used to formulate AmSiPU coatings. Surface characterization performed using XPS, AFM, and Attenuated Total Reflection Fourier Transformed Infrared Spectroscopy (ATR-FTIR) indicated the presence of both PDMS and PEG on the coating surface. The surface morphology of AmSiPU coatings were greatly affected by the compositional variations linked to pre-polymers. Several coatings showed excellent FR properties towards several model organisms indicating broad spectrum FR effectiveness. AmSiPU coatings had improved FR towards bacteria, diatoms, green algae, and barnacles when compared to A4-20 SiPU control. Also, many AmSiPU compositions displayed similar or better FR performance to latest commercial standards such as Intersleek® 1100 (IS 1100) and Hempasil® X3 (Hemp X3) during laboratory biological assays. More importantly, it is worth to note that incorporation of hydrophilic PEG component in to SiPU coatings did not negatively affect the FR performance towards any particular model organism tested; which was not the case for previous attempts to prepare PEG modified SiPU coatings. In future, select AmSiPU coatings should be included in field immersion trials to evaluate long term FR properties.

Highly hydrated surfaces have recently become attractive as antifouling surfaces given the thermodynamic and kinetic factors negatively affecting protein adhesion. Zwitterionic components and PEG are most commonly used for protein resistant materials. In order to obtain highly hydrated surfaces, several hydrophilically modified surface active pre-polymers based on PEG-PDMS and sulfobetaine-PDMS were investigated. Additionally, a small amount of non-reactive hydrophilic additives were also included in the coating formulations. Surface wettability of these SiPU coatings seemed to change rapidly from hydrophobic to hydrophilic (in a time scale of minutes). Coatings with PEG-PDMS side chains were efficient in FR of bacteria compared to those with sulfobetaine-PDMS. Several coatings also showed excellent diatom removal, comparable to commercial standards IS 1100 and Hemp X3. A marked improvement in microfouling release was observed for hydrophilically modified SiPU coatings compared to A4-20. Experimental coatings also showed good AF/FR properties towards barnacles and mussels. However, more sophisticated surface analysis is required to build strong conclusions related to surface characteristic vs. FR trends observed. Surface imaging using AFM in air and in water can be very useful techniques to investigate the existence of hydration layer. Also XPS experiments can be used to understand the surface morphology differences between coatings. Observing the wettability and surface energy after prolonged exposure to water would be helpful in future to understand the stability of the coatings.

Further exploration with amphiphilic and hydrophilic strategies to improve FR performance of SiPU coatings remain as the most prolific direction for the future. A study could be conducted to investigate the effects of non-reactive hydrophilic additive on FR performance of SiPU coatings. Effects of FR properties of A4-20 based formulation modified with hydrophilic additives with different molecular weight (MW), PEG chain density and additive concentration can be studied. Also designing siloxane resins with grafted PDMS-PEG or PDMS-zwitterionic chains and incorporating it in to SiPU coating system could be another possible route to obtain amphiphilic/ hydrophilic FR surface. Grafting could be performed via hydrosilylation of allyl PEG and allyl PDMS on to PDMS copolymer with silane groups on the backbone.

SiPU coatings with slight modification in solvent content provided two differently performing coating formulations towards mussel adhesion (both fresh water and marine mussels). The coating C4-20% displayed excellent AF/FR properties compared to A4-20%. The C4 formulations retained mussel FR up to 3 years, whereas FR performance of A4 coatings seemed to decline close to 1 year in field immersion with the only variability in the formulations attributing to the addition of ethyl-3-ethoxypropionate (EEP) into C4-20% formulation. The surface analysis conducted using X-ray photoelectron spectroscopy (XPS) suggested that self-stratification was affected by addition of EEP. Therefore, it would be important to understand the effect of EEP on long term FR properties of SiPU coatings in regard to mussels. An experiment can be designed to study the change in morphology and fouling release properties of C4-20% coating. The effect of coating curing condition can be studied by formulating C4 coatings and curing replicate panels under different conditions. For example, the same formulation can be subjected to several curing conditions; ambient curing, oven curing at elevated temperatures and curing under reduced pressure (vacuum oven) and elevated temperature. Also, the effect of immersion time can be studied as well. Coatings can be exposed to different immersion times in the pre-leaching tank (1 month, 3 months, 6 months, 9 months, and 12 months). In each case morphology of the coating can be analyzed using XPS, ATR-FTIR, contact angle and surface energy measurements. Then observed variations in morphology may be correlated to FR properties evaluated using laboratory biological assays.

Overall the versatility of modifying SiPU coating system to improve FR properties has been demonstrated. Throughout this work, multiple approaches were explored to tailor the surface properties of SiPU coatings which resulted in progress towards better FR performance. Novel approaches to fine tune the surface balance of hydrophilic and hydrophobic characteristics have led to broad spectrum FR properties during laboratory biological assays. Incorporation of silicone oil helped to prolong the service life of SiPU coatings in field immersion tests. Freshwater fouling release performance of SiPU coatings were evaluated for the first time, showing promise as viable candidate for contending with mussel fouling. So far the research and development efforts revolved around SiPU marine coatings show that it is an environmentally friendly, highly tunable robust coatings system with comparable FR performance to commercial standards with the added advantage of mechanical durability and toughness.

APPENDIX

Chapter 2. Supplemental Information

Table A1. 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 A2. 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 A3. *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 A4. *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 A5. 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 A6. *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 A7. *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 A8. 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 A9. *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 A10. 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 A11. 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 A12. *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 A13. 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 A14. 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 A15. 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 A16. 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

Chapter 5. Supplemental Information

Table A17. Detailed formulations for IPDI-M5KPDMS(10%)-550PEG(10%) pre-polymer portion of formulation 8

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

Table A18. Compositions of pre-polymers investigated during AmSiPU 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

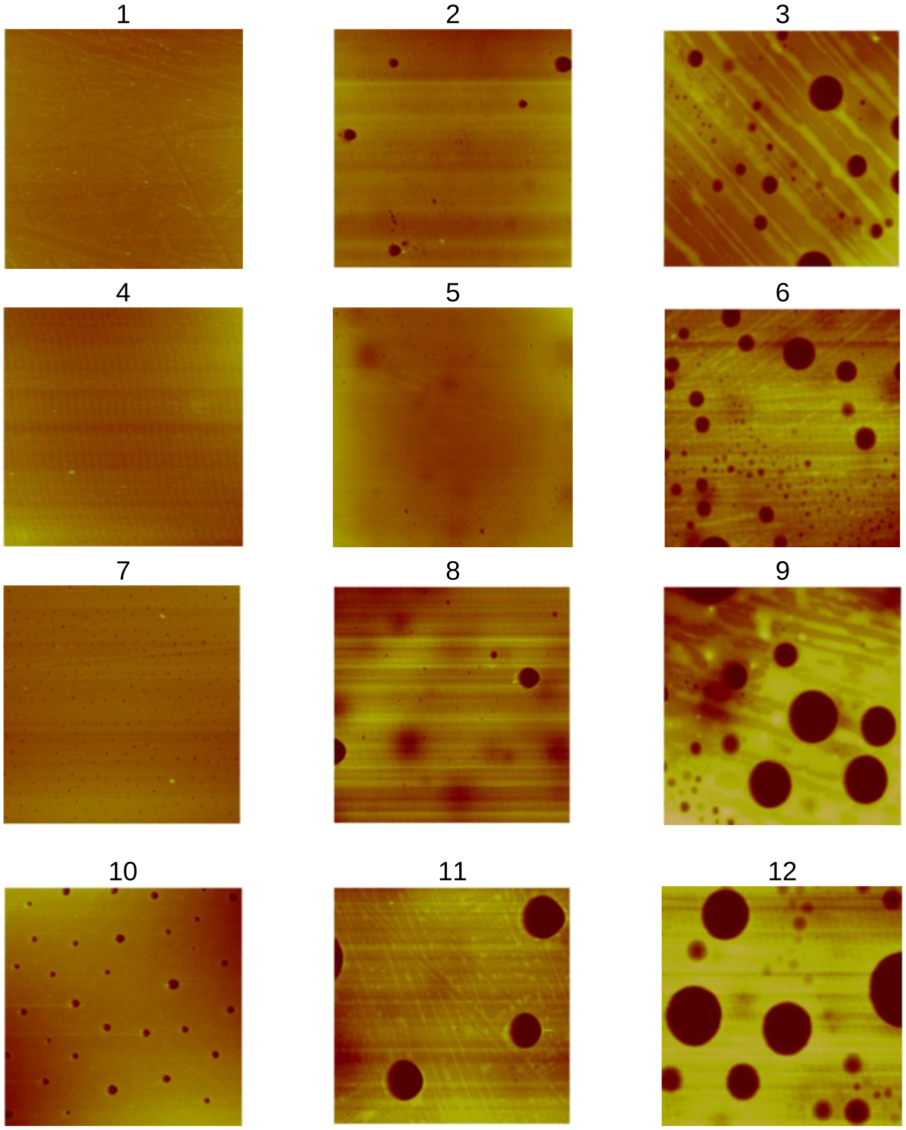

Figure A1. AFM height images for AmSiPU coatings

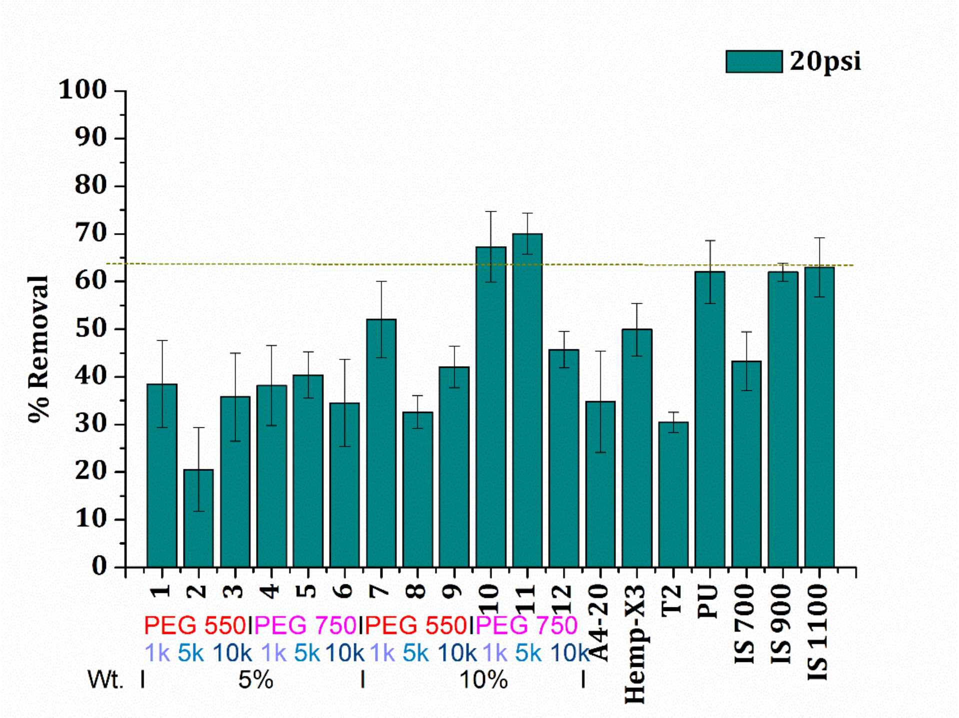

Figure A2. Percent removal of diatoms (*Navicula incerta*) from coatings

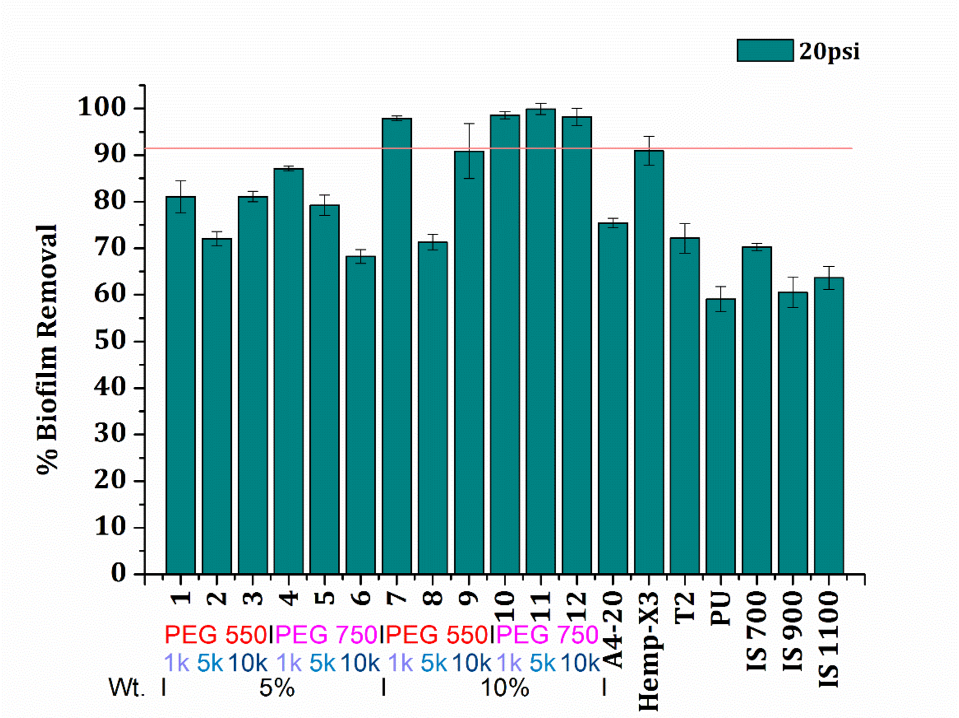

Figure A3. Percent removal of bacterial biofilm (*Cellulophaga lytica*) from coatings

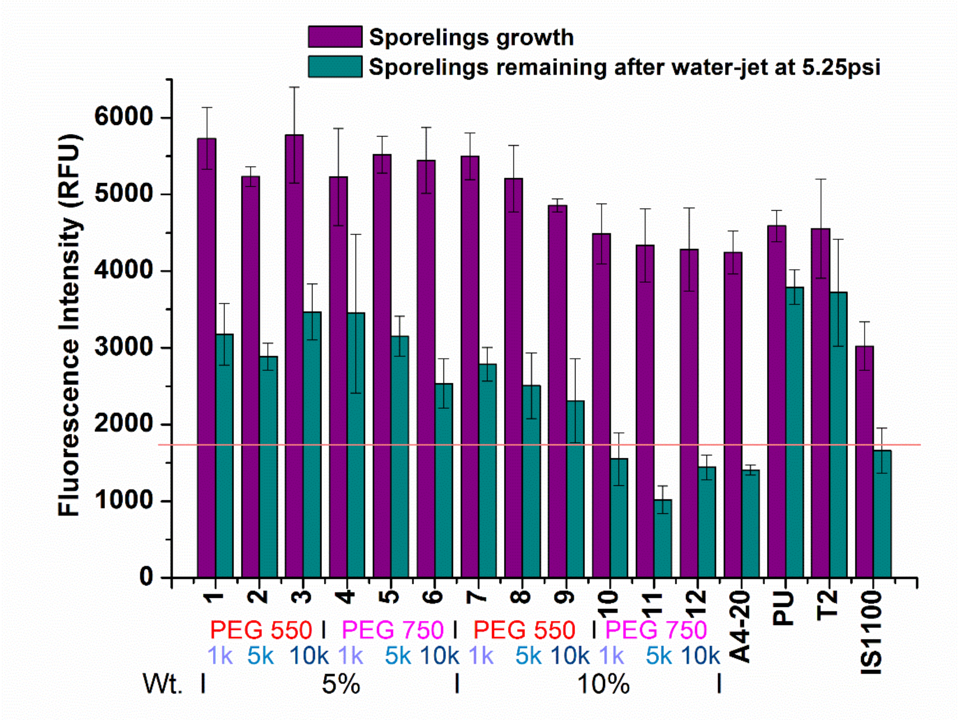

Figure A4. Macroalgae (*Ulva linza*) initial attachment and retention (i.e., biomass remaining) after water-jet treatment at 36 kPa pressure