SILOXANE-POLYURETHANE FOULING-RELEASE COATINGS BASED ON PDMS MACROMERS

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

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ABSTRACT

Sommer, Stacy Ann, Ph.D., Department of Coatings and Polymeric Materials, College of Science and Mathematics, North Dakota State University, April 2011. Siloxane-Polyurethane Fouling-Release Coatings Based on PDMS Macromers. Major Professor: Dr. Dean C. Webster.

Marine biofouling is the accumulation of organisms onto surfaces immersed in sea water. Fouling of ships causes an increase in hydrodynamic drag which leads to performance issues such as increased fuel consumption and a reduced top operating speed. Fouling-release (FR) coatings are one way that paints have been used in combating biofouling by allowing for the easy removal of settled organisms. Traditional FR coatings are silicone elastomers which are soft, easily damaged, and require a tie coat for adhesion to marine primers. Siloxane-polyurethane FR coatings have shown promise as FR coatings, providing enhanced durability and toughness, better adhesion to marine primers, and comparable FR performance to commercial coatings.

Preliminary studies were conducted to explore the use of PDMS macromers in the preparation of siloxane-polyurethane FR coatings. Attachment and removal of fouling organisms on the siloxane-polyurethane coatings based on PDMS macromers was comparable to commercial FR coatings. Extended water aging was also carried out to determine effects of extended water immersion on the fouling-release performance of the coatings. At up to four weeks of aging, the FR performance of the coatings was not affected.

Static immersion marine field testing was performed to determine the fouling-release performance of siloxane-polyurethane coatings prepared with PDMS macromers. The performance was found to be comparable to commercial

FR coatings for up to one year, including water jet removal of slimes, barnacle push-off removal, and soft sponging. The coatings showed good fouling-release performance until extremely heavy fouling was allowed to settle.

Underwater hull cleaning was conducted for one siloxane-polyurethane composition identified as a top performer from static field testing. The coating was easily cleaned of fouling with rotating brushes for six months. The cleaning capability of the coating was reduced when large barnacles and other extremely heavy fouling was present. A commercial FR coating became heavily damaged with brush cleaning while the siloxane-polyurethane coating remained mostly undamaged. With more frequent cleaning, it is suspected that siloxane-polyurethane coatings would show cleaning capability for longer periods of time.

Pigmentation of siloxane-polyurethane coatings based on difunctional PDMS and PDMS macromers was explored to investigate the effect on FR performance. Pigmentation with titanium dioxide caused a slight decrease in FR performance in some cases, but this was easily overcome by the addition of slightly more PDMS in the coating binder, thus illustrating the feasibility of siloxane-polyurethane coatings as effective, pigmented FR coatings.

Finally, the exploration of unique PDMS polymer architectures has been explored for the development of additional, novel, fouling-release coatings. The incorporation of end-functional PDMS homopolymer molecular brushes and branched PDMS macromers into siloxane-polyurethane fouling-release coatings shows promise for the development of unique coatings where improved FR performance may be obtained.

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DEDICATION

I dedicate my dissertation to my husband, Nick Sommer. You have always stood by me, even when it meant doing so in Fargo, ND. I am eternally grateful for your love and support; I look forward to raising children and growing old together.

I also dedicate my dissertation to my nieces and nephews: Caleb, Madison, Isabel, Angel, Arianna, and Jacoby. I hope that my influence persuades all of you to become part of the next generation of scientists.

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CHAPTER 1. GENERAL INTRODUCTION

1.1. Marine biofouling

Marine biofouling is the attachment of organisms onto surfaces immersed into sea water. The biofouling process has been described as occurring in four stages. The first stage of the biofouling process is the adsorption of an organic molecule conditioning film of proteins, polysaccharides, proteoglycans and other organic molecules.[1] This stage occurs within the first few minutes that a surface is immersed into natural waters.[2] This adsorption initiates the attachment of microbial life, as it contains nutrients essential for their survival.[3] The attached microorganisms form a coherent biofilm that contains algae, bacteria, fungi, and an adhesive, or sticky extracellular matrix.[1] Macrofouling attachment follows after formation of the biofilm, and may consist of soft fouling such as sponges and tunicates, or hard fouling such as tube worms and barnacles.[2] While each stage of fouling may colonize or dominate a surface eventually, the type of fouling that attaches is often influenced by what had settled previously.[4]

The complexity of the biofouling process and the diversity of the organisms which are known to attach to underwater surfaces make it difficult to prevent, even with modern technology. There are more than 4000 fouling organisms that have been identified worldwide, and they are dispersed throughout the world's ecosystems.[1] These organisms attach to surfaces through various mechanisms and adhesives, and this makes it very difficult to prevent their adhesion.[5] In the world, there are twelve unique ocean zones that have different temperatures, contain different nutrients, and are different in clarity.[6] Because of the globalization

of industry in today's modern world, and the transportation of goods throughout the world, a solution to biofouling must include one that is effective in all zones of the ocean, and against all of the known fouling organisms. Thus, there is continual need for the development of new methods of preventing biofouling, or reducing the effects it has on ocean going vessels.

Marine biofouling is problematic for ships, as it tends to accumulate on their hulls and causes a number of issues. The accumulation of fouling on today's ships increases hull surface roughness, and therefore, hydrodynamic drag.[7] This increased resistance as a ship moves through water can cause dramatic increases in fuel consumption, and a reduction in operating speed, and maneuverability.[8] Because of these detrimental effects on a ship's performance, biofouling costs the U.S. Navy an estimated $1 billion per year.[2] Furthermore, the adherence and subsequent release of organisms from a ship hull poses the threat of organism transport, which can lead to non-native or invasive species introduction.[9,10]

1.2. Methods of controlling biofouling on ships

1.2.1. Antifouling coatings

Historically, humans have explored a variety of methods for preventing the fouling of ship hulls. In early times, wooden hulls were protected with coverings of lead, copper, pitch, tar, wax, asphalt, oil, tallow, and other available materials.[1,11] When iron ships were introduced, the development of different systems was necessary, as the widely used copper sheathing accelerated the corrosion of the iron.[12] It was the use of iron ships which eventually led to the development of antifouling (AF) coatings after attempts of sheathing with many other metals, and

wooden, rubber or cork sheathing covered with metals were unsuccessful.[1] The first of these AF paints were "free-association" paints where varieties of toxins were dispersed in natural binding agents (linseed oil, shellac, tar, rosin). This broad description of an AF paint described most systems from that point on. However, many toxins and binder materials were explored, depending on the current technology and regional availabilities. Eventually, highly effective AF paints which contained broad spectrum biocidal triorganotin compounds were developed. Specifically, tributyltin (TBT) self-polishing copolymer paints became widely used in which TBT was bonded to a resin through an organotin-ester linkage and became slowly leached from the coating as those links were cleaved and the polymer eroded.[13,14] These paints were known to offer protection from fouling for upwards of five years, and were estimated to save the shipping industry $5.7 billion during the mid 1990s in fuel and by delaying ship dry dock and repaint.[15]

While TBT paints were successful at preventing fouling of ship hulls, their constant leaching of biocides into the environment was problematic.[1] Leaching of TBT into the environment, even at very low concentrations, was found to have detrimental impacts on non-target organisms. It is because of these multiple species negative impacts that TBT paints were to be removed from vessels by 2008. As alternatives, copper based paints, already in use, gained popularity following the ban of TBT. These paints contain copper salts as biocidal agents and booster biocides to aid in prevention of slime fouling which can be resistant to copper salts. While less so than TBT, these systems have also shown negative effects on natural life. In port areas where copper concentrations can be high due

to dense and extended docking periods, copper species in the water can cause negative effects, mostly, on microorganisms. However, many of the booster biocides, commonly organic, build up in the sediment and have been found to have greater impacts on local ecosystems. It is because of these negative effects that environmental agencies wish to remove toxins from marine paints and that non-toxic alternatives are being widely explored.[16]

1.2.2. Fouling-release (FR) coatings

The relatively recent push to develop a non-toxic alternative to AF coatings has focused a lot of attention on fouling-release (FR) coatings. These coatings minimize the adhesion of biofouling organisms through the use of a low surface energy (SE) material that prevents the formation of a strong adhesive bond.[17] Some of the most successful FR coatings have been based on silicone elastomers which are low in SE and modulus.[18] Both of these properties are important in determining release from a surface, as SE influences initial attachment to a surface and low modulus influences organism release by allowing peeling from the surface.[19] However, the elastomeric coatings that have been developed on this premise are soft and mechanically weak, which leads to their easy damage in the marine environment.[18] These coatings also do not adhere well to marine primers and often require the use of a tie coat to achieve satisfactory adhesion.[1] Additionally, their performance is often enhanced by the addition of non-reactive silicone slip agents which leach from the coating over time, into the marine environment.[20] While these slip agents are released at very low levels and known

to be typically non-hazardous, their gradual release from coatings can lead to the decrease of performance over time.

Siloxane-polyurethane coatings are a class of self-stratified FR coatings which attempt to address the shortfalls of traditional FR coatings based on silicone elastomers. As their name indicates, these coatings can provide the adhesive and tough properties of polyurethanes with the low surface energy of siloxanes which negatively influences bioadhesion.[21] The incorporation of a reactive silicone component (generally polydimethylsiloxane (PDMS)) into a polyurethane formulation allows for the formation of a self-stratified morphology during film formation, where the PDMS component migrates to the surface due to its low surface energy, and the polyurethane component forms the bulk of the coating and provides good adhesion to the marine primer.[22] Because of the reactive nature of the PDMS component, and the crosslinked polyurethane, this morphology is locked into place and is stable for immersion into sea water.[23]

The use of these types of coatings in the preparation of FR marine coatings is logical, as self-stratified coatings are used to combine two coating steps into one where coating properties typically from two distinct coating layers can be obtained in a single coating step.[24,25] Additionally, self-stratified coatings offer added benefits over two individual coating layers, as there is less risk of adhesive failure due to a higher degree of interaction between two systems which may not have bonded well as individual layers. In this case of self-stratification (siloxane-polyurethane coatings), the polyurethane component adds to the mechanical integrity of the coating, by offering toughness that is inherent to this class of

coatings, along with good adhesion to the marine primer. The PDMS component offers the low surface energy surface which is necessary in FR systems to minimize interaction between the coating surface and the fouling organisms. This type of coating system may replace the traditional FR coating system where a tie coat and top coat are applied. In this case, the polyurethane bulk may act as a tie coat between the PDMS and the epoxy marine primer, but an additional coating step is not required and the added toughness and durability of the polyurethane are also present.

1.3. Adhesion

Adhesion occurs through the following four mechanisms: chemical bonding, electrostatic interactions, mechanical interactions, and diffusion.[6] Ionic, covalent, dispersive, and dipolar bonding occurs at the interface to form strong bonds with the substrate. Electrostatic adhesion occurs through dipolar and ionic groups which interact electrostatically at the surface. Mechanical adhesion occurs through penetration of the surface, resulting in mechanical interlocking. Diffusion of adhesive into a coating's surface occurs by the creation of temporary voids by the movement of molecules at the surface. This allows for phase entanglement which helps an adherend bond with a surface.

Adhesion can be counteracted by addressing each of the interactions separately.[26] Chemical bonding at a surface can be discouraged by introducing non-polar and non-reactive groups which cannot interact with the adherend or by introducing mobile groups at the surface, making it difficult for adhesive bonds to form with the surface. Electrostatic adhesive interactions can be prevented by

eliminating the presence of heteroatoms, polar and ionic groups near the surface. Mechanical interactions can be overcome by creating a hard, smooth surface that is void of pores, even on the nanoscale. Similarly, diffusion-related adhesion can be overcome by creating a highly crosslinked surface that is composed of closely packed groups.

Adhesion to FR coatings is influenced by three main coating properties: surface energy, modulus, and thickness.[27] Initial work which focused on the adhesion of blood proteins to varying surfaces identified a surface energy range (20-30 mN/m) in which adhesion to a surface was minimized.[28] Modulus is also important in determining release from a surface where a low modulus is desired for release.[20] The geometry of an adhesive joint and the thickness of a release coating also play an important role in determining release as they can affect the mode of release from a surface.[29] Kendall's work has been related to the pull-off adhesion of an epoxy-adhered metal stud from the surface of a coating, and is represented in the equation (1.1) below where P_c is the critical pull-off force from a coating, t is the coating thickness, w_a is Dupré's work of adhesion between the coating and the metal stud, K is the coating's bulk modulus, and a is the radius of contact.[30] The work of adhesion (w_a) as defined by Dupré, is shown in equation (1.2) below where γ_s is the surface energy of the coating, γ_l is the surface tension of the adherent liquid, and γ_{sl} is the interfacial tension between the coating and the adherent liquid. When w_a is negative, adhesion does not occur.[31] Much of the work

$$P_c = \pi a^2 \left(\frac{2w_a K}{t}\right)^{1/2} \tag{1.1}$$

$$w_a = \gamma_s + \gamma_l - \gamma_{sl} \tag{1.2}$$

in the field of FR coatings is based on the application of this fundamental relationship in fracture mechanics. This has formed the foundation for FR coating research, and FR coatings are generally formulated with a targeted high thickness, low modulus, and low surface energy.

Surface energy is the excess energy contained by surface molecules compared to bulk molecules and it is indicative of the ability of a surface to interact with another material.[32] While an important material property, surface energy is difficult to measure directly and is commonly measured through the use of contact angle measurements where the wetting angle of a liquid on the material in question is measured. A schematic of the contact angle measurement is shown in Figure 1.1 and is represented by Young's equation (1.3) where θ is the liquid wetting angle on the solid, γ_{sl} is the interfacial tension between the solid and liquid, γ_{lv} is the interfacial tension between the liquid and the surrounding vapor, and γ_s is the surface energy of the solid.[33] Over the years, many methods have been developed for determining the surface energy of a solid, and many of these have been based on the study of liquid wetting on their surfaces. Fox and Zisman found

$$\gamma_s = \gamma_{sl} + \gamma_{lv} \cos\theta \tag{1.3}$$

that the cosine of the wetting angles of different liquids could be plotted to yield a linear relationship. The extrapolation of this plot to the point where perfect wetting occurred ($\cos\theta=0$) was used to determine the critical surface tension of the solid, where it was assumed to have the same surface tension as the liquid by which it was perfectly wet.[34,35] Another method was developed by Owens and Wendt to determine the surface energy of a solid using only two liquids.[36] This method is

based on the idea that surface energies are composed of polar and dispersive components. Two liquids and their contact angles with the solid are used in determining the surface energy of the solid through the calculation of a geometric mean. This is a common method for the determination of a solid surface energy.

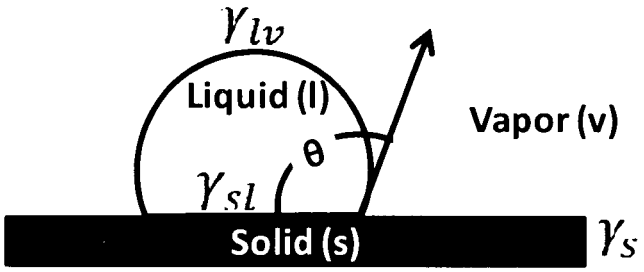


Figure 1.1. Wetting angle schematic where the contact angle between a liquid and a solid is measured where θ is the liquid wetting angle on the solid, γ_{sl} is the interfacial tension between the solid and liquid, γ_{lv} is the interfacial tension between the liquid and the surrounding vapor, and γ_s is the surface energy of the solid.

1.4. Polymers used in release coatings

As previously stated, FR coatings are commonly based on a low surface energy material which minimizes the interaction of an adherend with the surface and allows for easy removal from a surface. There are predominantly two polymer types that offer low surface energies; these have been extensively researched for these applications and they include fluoropolymers and silicone polymers. The FR systems in place today are generally based on silicone polymers, specifically polydimethylsiloxane (PDMS).[37] This is in part due to the low surface energy of

silicone-based polymers, but also due to their lower modulus and reduced cost compared to their fluoropolymer counterparts. Additionally, while PDMS also has a low solubility parameter, the solubility of fluoropolymers in typical organic solvents is low, while silicone polymers are typically soluble in most organic solvents, which eases coating formulation.

1.4.1. Polydimethylsiloxane (PDMS)

A common silicone polymer, PDMS is widely used throughout polymer science applications due to its wide commercial availability, inert chemical nature, low toxicity, biocompatibility, oxidative and thermal stability, low modulus, and handling ease.[38,39] The polymer backbone is composed of alternating silicon and oxygen atoms where the silicon atom has two attached methyl groups. The basic polymeric structure of PDMS is shown in Figure 1.2. The inherent flexibility of these polymers is due to the flexible polymer backbone composed of silicon-oxygen bonds which have wide bond angles.[40,41] This flexibility enables rotation along the polymer backbone and allows for the adaptation of thermodynamically favorable configurations, which contributes to the low surface energy of these types of polymers compared to organic polymers.[42] This unique flexibility and the polymer's lack of polarity are the source of its many unique properties and broad application. Another unique property which PDMS possesses is an extremely low glass transition temperature (T_g, -120°C) which contributes to its ease of use (oily liquid at room temperature), and flexibility.

Polydimethylsiloxane and other silicone polymers have been widely used in coating science to modify surfaces, polymers, or resins to enhance properties for

specific applications. Purely silicone coatings have also been used, as they can impart the same properties as their thermoplastic counterparts.[43] However, because these materials can be costly or require high temperature or extended curing times, the modification of other materials with silicones has been broadly explored. This approach allows for tailored properties, as the characteristics of one resin can be combined with that of silicones for a "best of both worlds" type of product. However, because of the unique properties of silicone resins, and their low solubility parameter, the combination of these materials with distinctively different materials can be challenging. Some examples where silicones have been used to modify other types of polymers, resins or surfaces are the following: silicone modified alkyds for improved exterior durability[43], silicone modified polyester and acrylic resins for coil coatings[43], silicone modified epoxy resins[44], improved abrasion resistance in melamine-formaldehyde coatings[45], and the toughening of polycarbonate[46]. PDMS itself can also be crosslinked to form silicone elastomers which have properties desired from PDMS that can also be moderately tailored for specific applications.

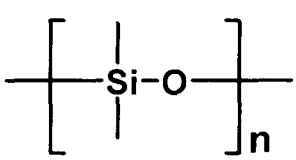


Figure 1.2. Repeat unit of PDMS polymers where the repeat unit is composed of alternating oxygen and silicon atoms.

The use of silicone polymers in the modification of resins, polymers or surfaces generally requires the presence of at least one functional group on the silicone polymer to allow it to interact with other chemical species. Therefore, silicone polymers are often prepared with organofunctionality to improve their utility in polymer science. Some examples of a few functionalities which silicones have been prepared with include the following: silicon hydride[47], nitrile and epoxy[48], acrylate[49], and vinyl ether[50]. Even biocidal moieties such as quaternary ammonium salts have been introduced onto polysiloxanes.[51] The functionality of these polymers is generally introduced as pendant groups, on both polymer termini, or on single polymer termini, depending on the application. [42] The functionality can be obtained by the polymerization of functionalized siloxane monomers (pendant functionality), or the use of an end blocking agent during polymerization (end functional). Often, the final functionality is obtained through further reaction once a polymer is prepared.

1.4.2. PDMS macromers

Macromonomers, or macromers, are polymers which possess functionality on a single end of the polymeric chain.[52] A linear polymer possesses one reactive chain end and one that is unreactive. A typical macromonomer is synthesized by initiation using a non-functional initiator, and selective termination of polymerization using a functional terminating species. Anionic polymerization and other controlled or "living" polymerization techniques lend themselves to this type of synthetic approach. Specifically, polysiloxane macromers can be prepared through the living anionic polymerization of the cyclic siloxane monomer hexamethylcyclotrisiloxane

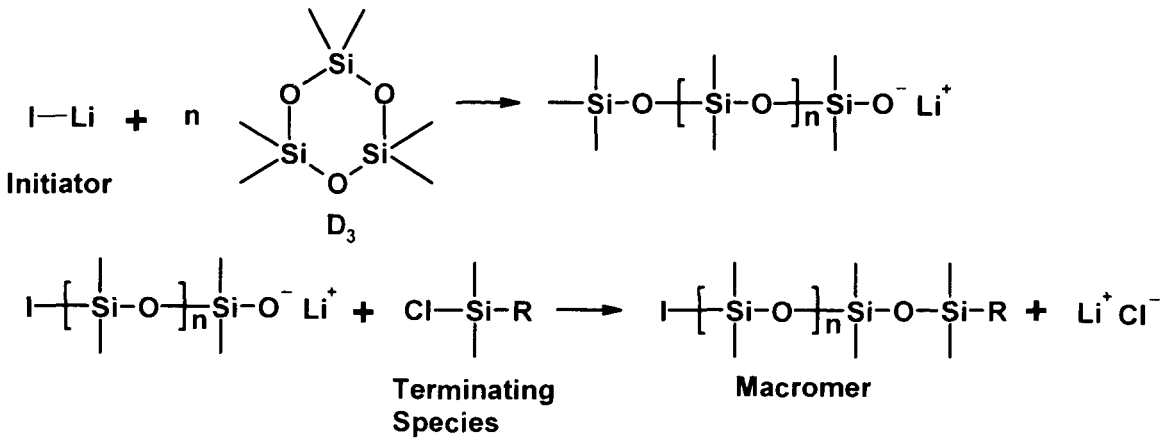
(D_3).[53] Initiation is carried out using an organolithium or lithium silanolate compound. The termination of this living polymerization using a functional chlorosilane agent imparts functionality on the polymer chain end.[54] A general synthetic scheme for this type of polymerization is shown in Scheme 1.1 where the initiator is a lithium base.[55] A different approach where a functional initiator was used to obtain a functional chain end, and a non-functional terminating species was used has also been reported.[56] Regardless of synthetic approach, the molecular weight of the macromers is controlled by the ratio of initiator to monomer. Equations (1.5), (1.6), (1.7), and (1.8) show the method for determining the appropriate amounts of reagent to obtain the proper molecular weight and functionality of PDMS macromers where MW_p is the molecular weight of the polymer (macromer), MW_i is the molecular weight of the initiating species, MW_m is the molecular weight of the monomer, n is the number of repeat units per monomer unit, $Mass_m$ is the mass of monomer needed (g), $Mass_p$ is the desired mass of polymer (g), mol_m is the moles of monomer, mol_p is the moles of polymer, mol_i is the moles of initiator, $Mass_t$ is the mass of terminating species, mol_t is the moles of terminating species, and MW_t is the molecular weight of the terminating species.

$$Target\ MW_p = MW_i + (MW_m * n) \tag{1.5}$$

$$Mass_m = \frac{Mass_p}{Target\ MW_p} * n * mol_m * MW_m \tag{1.6}$$

$$Mass_i = \frac{Mass_p}{Target\ MW_p} * \frac{1\ mol_i}{1\ mol_p} * MW_i \tag{1.7}$$

$$Mass_t = \frac{Mass_p}{Target\ MW_p} * \frac{2\ mol_t}{1\ mol_p} * MW_t \quad (1.8)$$



Scheme 1.1. Synthetic scheme for the preparation of a PDMS macromer, where the initiating species can be an organolithium reagent or a lithium silanolate, and the terminating species imparts the functionality onto the polymer chain end.

The final functionalization of macromers can be carried out directly during the termination of polymerization, or performed using additional synthetic procedures. For instance, if silicon-hydride functionality is obtained during polymerization termination, hydrosilylation can be carried out to obtain a different functionality. Hydrosilylation involves the addition of silicon-hydride to a multiple bond such as a carbon-carbon double bond.[57] A number of hydroslylation reactions have been explored, and many catalysts have been prepared to achieve various functionalities and/or purities.

The use of PDMS macromers in the formulation and preparation of siloxane-polyurethane FR coatings was based on a combination of ideas. The first is that similar coating systems based on telechelic PDMS where two primary amine groups reacted the PDMS into the polyurethane bulk showed good FR

performance in laboratory bioassays used for screening FR performance.[58] It is well accepted that silicone elastomer based fouling-release coatings often contain silicone oils which are included as slip agents to slowly leach from the coating surface and help create weak boundary layers to help prevent strong organism attachment.[59,60] It was hypothesized that the use of silicone polymers where a single reactive chain end anchored the polymer chain to the polyurethane bulk may enhance the FR performance of siloxane-polyurethane coatings through a similar mechanism. Additionally, because the silicone polymers in this case are reactive, their supply within the coating should not deplete over time, as has been observed in silicone elastomer coatings, which leads to performance depletion and coating embrittlement. The synthesis of PDMS macromers and their use in siloxane-polyurethane FR coatings is the focus of this thesis.

1.5. Assessment of FR performance

1.5.1. Laboratory screening

The development of new coating systems for FR applications is a difficult task in which many coating compositions need to be explored, but testing on marine vessels limits the number of samples that can be easily tested, the timeframe for gathering meaningful data can be lengthy, and significant resources are required.[61] At North Dakota State University (NDSU), in the labs at the Center for Nanoscale Science and Engineering (CNSE), there are many tools available for combinatorial and high throughput polymer synthesis, coating formulation, coating screening, and AF and FR laboratory assays where a multitude of coatings can be rapidly prepared and screened for performance as marine coatings. An automated

surface energy tool is used to measure water and methylene iodide contact angles on the surface from which surface energy is calculated.[62] Pseudobarnacle (PB) adhesion is a pull-off adhesion measurement in which the adhesion of an epoxy glued metal stud to a surface is measured.[63] This measurement is used to preliminarily and rapidly assess the release properties of a surface. Typically if a coating does not have a low surface energy or low PB adhesion, its screening as a FR coating is discontinued.

For those coatings which possess low surface energy and PB adhesion, screening is carried out using a suite of high throughput bioassays which help determine the adhesion of fouling organisms to fouling-release surfaces. These include assessment with marine bacteria, marine microalgae diatoms, live adult barnacles, and macroalgal zoospores. Negative leachate toxicity is always confirmed prior to the analysis using marine organisms to eliminate false results.[64] In the bacterial FR assay performed at NDSU, the biofilm retention, retraction, and removal bioassays where bacterial settlement, surface wetting, and water jet removal of common marine fouling bacteria (*C. lytica* and *H. pacifica*) is assessed.[65-67] In the microalgae diatom assay also performed at NDSU, the attachment and water jet removal from coating surfaces is assessed.[68] Live adult reattached barnacles are used to assess the removal of shell fouling from coating surfaces.[69] This analysis is also performed at NDSU. The attachment and water jet removal of macroalgae zoospores is assessed through an assay performed at the University of Birmingham.[70-72] The use of these assays allow for the rapid

screening of FR performance to determine which coatings provide the best release of fouling organisms.

1.5.2. Marine testing

The laboratory assessment of FR performance of coatings is a useful tool in rapidly screening the performance of coatings in a laboratory setting. However, because there are more than 4000 species that are known to cause marine fouling[1], it is not reasonable to use *only* laboratory testing to screen the performance of AF or FR coatings. Therefore, ocean testing is required to gain experience with how a coating performs in the true marine environment, where many marine fouling organisms are present and fouling occurs naturally.[73] Additionally, testing in the marine environment exposes coatings to natural physical, chemical and biological parameters which are difficult to reproduce in a laboratory. Marine testing is generally performed at field testing sites supported by the Office of Naval Research where standard tests are performed to assess the FR performance of these coating systems. Typically, water jetting is performed to assess slime and soft fouling removal from the coating surfaces. After the settlement of hard fouling, appropriately sized adult barnacles are removed by lateral push off and their removal forces are measured to gauge the removal of shell fouling from the coatings (ASTM D 5618). It is through this static immersion testing that many of the best coatings are selected for further analysis which may include patch testing on actual marine vessels.

1.6. Research scope and purpose

The purpose of this research was to formulate siloxane-polyurethane FR coatings for marine applications. A tougher, more durable coating system which

possesses FR performance similar to commercial coatings is desired, and that was the focus of this research. The exploration of PDMS macromers and their use in FR coatings is the primary theme throughout this work. These polymers were synthesized using living anionic polymerization and formulated into siloxane-polyurethane coatings which contained a hydroxyl functional polymer, polyisocyanate resin, catalyst, and solvent. The polymers and coatings were characterized using various methods such as gel permeation chromatography (GPC), nuclear magnetic resonance spectroscopy (NMR), water contact angle (WCA), surface energy (SE), and pseudobarnacle (PB) adhesion. Laboratory biological assays and marine testing were used to screen the FR performance of the coatings. Underwater cleaning was also explored for these systems to evaluate their FR performance and explore the use of underwater cleaning tools as a means of controlling fouling accumulation for these systems. Pigmentation of siloxane-polyurethane FR coatings containing both PDMS macromers and difunctional PDMS was explored to determine the effects of pigmentation on the FR performance and properties of the coatings. And finally, unique PDMS polymer architectures where PDMS macromers were used as polymeric precursors were prepared so they can be used to prepare coatings and their FR performance can be evaluated for potential use as FR coatings.

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CHAPTER 2. A PRELIMINARY STUDY ON THE PROPERTIES AND FOULING-RELEASE PERFORMANCE OF SILOXANE-POLYURETHANE COATINGS PREPARED FROM PDMS MACROMERS

2.1. Introduction

Marine biofouling is an ancient problem which has troubled humans since seagoing vessels first were developed,[1] and more than 4000 fouling organisms have been identified worldwide.[2] Biofouling is an expensive problem, and is estimated to cost the US Navy $1 billion annually.[3] Such fouling can affect a ship's maneuverability and cause a drastic increase in fuel consumption.[4] Additionally, fouled ships can transport organisms across ecosystems, posing a threat of introducing non-native species into sensitive ecosystems.[5,6] Biocidal paints are used to combat biofouling, but often the biocides released into the marine environment have been found to have negative effects on non-target organisms.[4,7,8] While effective in reducing biofouling, recent regulatory changes have increased interest in replacing biocidal antifouling paints with a completely non-biocidal alternative. Fouling-release coatings have attracted a lot of attention for this reason. While they do not inhibit organism settlement, they provide a surface from which settled organisms can be easily released, either by the hydrodynamic forces created as a vessel moves through the water or gentle mechanical cleaning.[9]

Traditional fouling-release coatings have been mostly composed of silicone elastomers, which are effective release coatings due to their low surface energy and low elastic modulus. However, they can be easily damaged in the rugged

marine environment due to their lack of mechanical strength, and they do not adhere well to marine primers.[2] More recently, siloxane-polyurethane coatings prepared using PDMS have been researched as fouling-release coatings because they couple the toughness and good adhesion of polyurethanes with the low surface energy of siloxanes. [10] These coating systems are prepared through the formulation of coatings containing both a polyurethane component and a reactive PDMS component. During application and film formation, self-stratification occurs within the coating system, driven by the incompatibility of the PDMS and polyurethane components. As a result of the low surface energy of the siloxane component, it migrates to the surface of the coating, resulting in a tough polyurethane system with a siloxane surface that can provide fouling-release properties.[11] The morphology of the coating is then locked into place as crosslinking occurs, and reactive groups on the PDMS anchor it in the polyurethane coating bulk to prevent rearrangement of the system when subjected to immersion in aqueous marine environments.[12]

Previous work with siloxane-polyurethane coatings has demonstrated their promise as fouling-release coatings when analyzed by laboratory assays using known marine fouling organisms.[13] In the referenced work, PDMS with multiple reactive groups was used in the formulation of coatings which showed good release of organisms, similar to silicone rubbers that were tested as controls. In this work, monohydride terminated PDMS macromers were synthesized through living anionic polymerization of a cyclic siloxane monomer, which has been described previously.[14,15] Functionalization was carried out by hydrosilylation of

the macromer with a protected allylamine, followed by deprotection[16] to yield an aminopropyl terminated PDMS macromer which was formulated into siloxane-polyurethane coatings. Four macromer molecular weights were explored (1,000, 5,000, 10,000, and 15,000 g/mol), as well as two loading levels (5% and 10% weight). The properties of the coatings were characterized for pseudobarnacle adhesion, water contact angle and surface free energy before and after 21 days of water immersion.

The purpose of this study was to explore the fouling-release performance of siloxane-polyurethane coatings prepared using PDMS macromers. A series of assays were performed to gauge the performance of these coatings on a laboratory scale. Pseudobarnacle pull-off adhesion was measured,[17] and the interaction of known biofouling organisms with the coating surfaces was examined by biofilm retention and release assays. Microorganisms (bacteria, a diatom, and a unicellular alga) were used to study the coating performance, as they are typically the first organisms to appear on an underwater surface, and are responsible for forming a microbial slime layer on a ship's hull. It is important to assess the strength of adhesion of these slimes as they are difficult to remove from silicone fouling-release coatings[1] and are responsible for a substantial increase in hydrodynamic drag[18] *Cellulophaga lytica* (*C. lytica*), a marine bacterium and known biofouling organism, was used to determine biofilm retention on the coating surfaces.[19] *Navicula incerta* (*N. incerta*), a unicellular alga (diatom) was used in water jetting assays where attachment to and removal from the experimental coating was measured. Diatoms are important test organisms for this type of study,

as they attach and form adherent biofilms on hydrophobic surfaces including silicone fouling-release coatings.[20-22] *Ulva linza* is a green seaweed, which reproduces by production of spores that rapidly develop into sporelings (young plants). Sporelings were used in a water jetting assay to assess fouling release performance.[23] Sporelings of *Ulva* have been shown to adhere weakly to silicone-based fouling-release coatings.[20,24,25] Finally, a live barnacle reattachment study was used to gauge the removal of live barnacles (*Amphibalanus amphitrite)* from the surface of the experimental coatings after being reattached to the coatings for 14 days.[26]

2.2. Experimental

2.2.1. Materials

Hexamethylcyclotrisiloxane (D_3) and dimethylchlorosilane (DMCS) were received from Gelest Inc. Inhibitor-free tetrahydrofuran (THF), acetylacetone (2,4-pentanedione, PD), lithium trimethylsilanolate (LTMS), Allyl-HMDS (*N*-Allyl-*N*,*N*-bis(trimethylsilyl)amine), ethyl 3-ethoxypropionate (EEP) and Karstedt catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex) were received from Sigma-Aldrich. Stabilized THF was received from VWR International. Tolonate® IDT 70B (IDT) was received from Rhodia. Methyl amyl ketone (MAK) was received from Eastman Chemical. Dibutyltin diacetate (DBTDAc) was received form Fluka. Tone™ polyol 0305 (PCL) was received from Dow Chemical. Intergard® 264 primer was received from International Paint and prepared according to manufacturer's specifications.

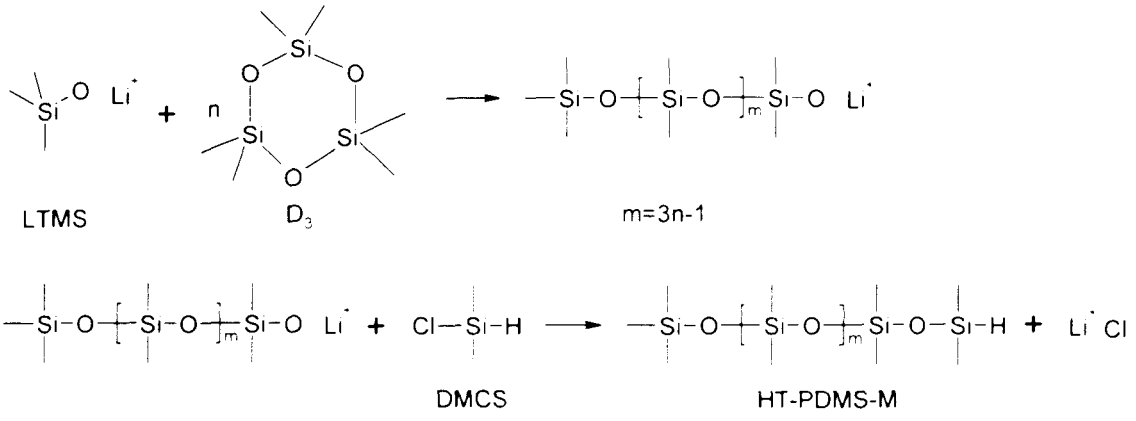
Standard coating systems were formulated for comparative analysis in the biological fouling-release assays. Intersleek® 700 (IS 700) was prepared according to manufacturer's specifications. Silastic® T2 (T2) was prepared according to manufacturer's specifications as well, and was thinned using methyl isobutyl ketone (MIBK) to a pipettable viscosity. Dow Corning® 3140 (DC) was used as supplied, and was thinned to a pipettable viscosity using MIBK. A control coating polyurethane coating system, formulated without the inclusion of siloxane was also included in the analysis.

The marine bacterium *C. lytica* was generously provided by Dr. Michael Hadfield of the Kewalo Marine Laboratory, University of Hawaii. The marine diatom *N. incerta* was generously provided by the University of Birmingham, UK. Reproductive plants of *U. linza* were collected from Llantwit Major, Glamorgan, Wales, UK (52° 23' N; 3° 30'W). Artificial seawater (ASW) was prepared by dissolving 38.5g of sea salts (Sigma-Aldrich) into 1L of deionized water. Bacterial biofilm growth medium (BGM) consisted of 0.1g yeast extract and 0.5g of peptone per 1L of ASW. Algal growth medium (F/2) consisted of 1L of ASW supplemented with nutrients to generate Guillard's F/2 medium.[21,27] BGM, F/2 and ASW were filter sterilized with 0.2 micron vacuum-cap filters. Crystal violet powder, 33% glacial acetic acid and dimethyl sulfoxide (DMSO) were used as received (VWR International).

2.2.2. PDMS macromer polymerization

Polydimethylsiloxane macromers with terminal monohydride functionality were prepared by the ring opening anionic polymerization of D_3 in THF. The

synthetic procedure for the PDMS macromer synthesis is shown in Scheme 2.1. For the polymerization, D_3 was dissolved in THF (inhibitor free) at a concentration of 50% by weight. The solution was degassed by bubbling nitrogen (N_2) gas through it for 15 minutes, while stirring the solution with a magnetic stir bar. LTMS salt was added to the solution to initiate polymerization at room temperature. The amount of LTMS added was varied in molar ratios to D_3 to achieve four target molecular weights (1,000, 5,000, 10,000, and 15,000 g/mol). After 24 hr, the polymerization was terminated by the addition of DMCS at 2-5°C. The terminating agent, DMCS, was added in excess (100% molar) to ensure termination of all polymer chain ends, resulting in monohydride functionality. Table 2.1 summarizes the amounts of D_3 monomer solution, LTMS initiator, and DMCS terminating agent that were used for the synthesis of PDMS macromers. The solutions were rotary evaporated to remove THF and a lithium chloride lithium chloride salt precipitate formed. The lithium chloride precipitate was removed by vacuum filtration to yield a clear, monohydride terminated PDMS macromer (HT-PDMS-M).



Scheme 2.1. Room temperature ring opening anionic polymerization of D_3 using LTMS as an initiator to yield monohydride terminated PDMS macromer.

Table 2.1. Amounts of D_3 solution, LTMS, and DMCS used in the synthesis of PDMS macromers with monohydride functionality.

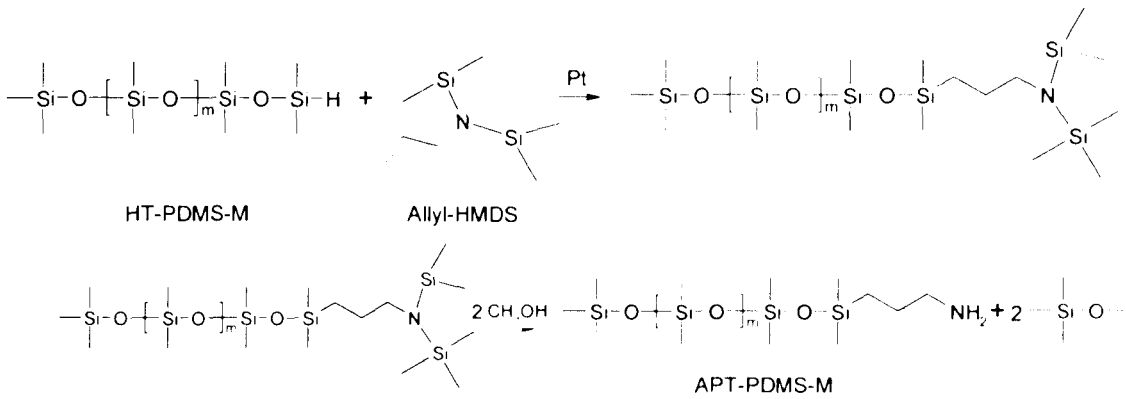
Theoretical MW (g mol^{-1})	D_3			LTMS		DMCS	
	Solution (g)	Mass (g)	mmol	Mass (g)	mmol	Mass (g)	mmol
1,000	100.0	50.0	220	4.87	50.8	9.6	101.5
5,000	100.0	50.0	220	0.96	10.0	1.9	20.1
10,000	100.0	50.0	220	0.48	5.0	0.9	9.9
15,000	100.0	50.0	220	0.32	3.3	0.6	6.7

2.2.3. PDMS macromer functionalization

A protected allylamine, allyl-HMDS, was added to the HT-PDMS-M. Hydrosilylation was carried out at 60°C in the presence of Karstedt catalyst of which 1 drop of solution in xylene was added. Table 2.2 summarizes the reaction times and reagents used for the hydrosilylation reactions. The products of the hydrosilylation reactions were called disilazane terminated PDMS macromers (DT-PDMS-M). The primary amine groups of the DT-PDMS-M were deprotected by washing with methanol (30ml) to yield aminopropyl terminated PDMS macromers (APT-PDMS-M). The synthetic procedure for functionalization of the PDMS macromers is shown in Scheme 2.2.

Table 2.2. Reaction times and reagents used for the functionalization of PDMS macromers through a hydrosilylation reaction of monohydride terminated PDMS macromers with allyl-HMDS.

Theoretical MW (g mol^{-1})	HT-PDMS-M (g)	Allyl-HMDS		Reaction Time (hr)
		Mass (g)	mmol	
1,000	33.3	12.5	62.0	22
5,000	38.5	5.3	26.3	22
10,000	39.2	2.4	11.9	22
15,000	39.5	2.0	9.9	22



Scheme 2.2. Functionalization and deprotection of PDMS macromers through hydrosilylation of monohydride terminated PDMS with allyl-HMDS to yield aminopropyl terminated PDMS macromers.

2.2.4. Characterization of PDMS macromers

2.2.4.1 Symyx® Rapid GPC: High-throughput gel permeation chromatography (GPC) was performed, relative to polystyrene standards, to determine the approximate molecular weight of the PDMS macromers. Solutions of the macromers were prepared at 2mg ml^{-1} in stabilized THF prior to analysis. The analysis was performed on a Symyx® Rapid GPC with an evaporative light scattering detector (PL-ELS 1000), 2xPLgel Mixed-B columns (10μm particle size) and a flow rate of 2.0 ml min^{-1}.

2.2.5. Siloxane-polyurethane coating formulation

Polyurethane (PU)-PDMS coating formulations were prepared using the APT-PDMS-Ms, isophorone diisocyanate trimer (IDT), a polycaprolactone polyol (TPCL), DBTDAc as a catalyst, PD as a pot-life extender and MAK and EEP as solvents. The APT-PDMS-M (30% in EEP), PCL polyol (90% in MAK) and DBTDAc (1% in MAK) were used as solutions for formulation purposes while Tolonate IDT 70B was used as supplied (70% in butyl acetate). A Symyx® Coating

Formulation System equipped with a liquid handling robot was used for preparation of the formulations. The coatings were formulated with a 1.1:1 ratio of isocyanate to hydroxyl and amine equivalents. The coating formulations are outlined in Table 2.3 with reagent quantities for approximately 10 grams of total formulation. The coating formulations were prepared by first mixing the APT-PDMS-M solution with IDT for 1 hour. The PD was added and the formulation was mixed. The addition of PCL polyol and DBTDAc solutions followed in that order. The coating compositions are summarized in Table 2.4.

Table 2.3. Coating formulation recipes for PU-PDMS coatings formulated with APT-PDMS-Ms of four theoretical molecular weights, IDT, TPCL, and DBTDAc.

Coating ID	30% APT-PDMS-M in EEP (g)	Tolonate IDT 70B (g)	90% PCL polyol in MAK	1% DBTDAc in MAK
1	1.08	6.03	2.21	0.10
2	2.17	5.77	2.08	0.10
3	1.08	5.98	2.21	0.10
4	2.16	5.68	2.08	0.10
5	1.08	5.97	2.21	0.10
6	2.16	5.66	2.08	0.10
7	1.08	5.97	2.21	0.10
8	2.16	5.66	2.08	0.10
9 (PU)	0.00	6.29	2.33	0.10

2.2.6. Siloxane-polyurethane coating preparation and curing

The panels used in biological testing (adhesion of barnacles and diatoms) were aluminum Q-panels® (4 x 8 in., 0.6mm thickness, type A, alloy 3003 H14, obtained from Q-lab) that had been primed via air-assisted spray with Intergard® 264 at a thickness of 70-80μm. The coatings used for pseudobarnacle adhesion and surface energy analysis were applied to unprimed aluminum Q-panels® which had been cleaned with acetone and xylenes. The coating formulations were

deposited onto the Q-panels® using a liquid dispensing robot and pipet and then drawn down using an adjustable, robotic doctor blade (10 mil gap thickness) onto the aforementioned primed/unprimed aluminum Q-panels® in an array format using a Symyx® Coating Application System. One patch of each coating formulation was applied to each Q-panel®. Several replicates were made of the array Q-panels®, to allow for several different tests to be performed.

Table 2.4. Dry coating composition of PU-PDMS coatings formulated using APT-PDMS-M. As shown in the table, eight experimental coatings were prepared, with four different APT-PDMS-M and two different loading levels of APT-PDMS-M.

Coating ID	Theoretical PDMS MW (g mol^{-1})	Mass % of Solids			Total Solids	DBTDAc (based on solids)
		PDMS	IDT	PCL Polyol		
1	1,000	5%	64%	31%	69%	0.015%
2	1,000	10%	61%	29%	65%	0.015%
3	5,000	5%	64%	31%	69%	0.015%
4	5,000	10%	61%	29%	65%	0.015%
5	10,000	5%	64%	31%	69%	0.015%
6	10,000	10%	61%	29%	65%	0.015%
7	15,000	5%	64%	31%	69%	0.015%
8	15,000	10%	61%	29%	65%	0.015%
9 (PU)	---	0%	68%	32%	75%	0.015%

The coatings for bacterial, diatom and *Ulva* assays were manually dispensed (250µL per well) using a repeat volume pipette into 24-well polystyrene plates in which a primed aluminum disc was adhered at the base of each well. The siloxane-polyurethane coatings and polyurethane control were cured at ambient conditions overnight and then oven cured at 80°C for 45 minutes the following morning. Standard coatings were also prepared in 24-well plates, but curing was

performed under ambient conditions for 24 hr (7 days for DC 3140) and the samples were not oven cured.

2.2.7. Characterization of siloxane-polyurethane coating physical properties

2.2.7.1. Contact angle and surface energy: Surface energy measurements were carried out using a Symyx® Coatings Surface Energy System on which the contact angles of water and methylene iodide (MI) on the coating surfaces were measured. Three droplets were individually placed on the coating surface, a photo was taken by a CCD camera and automated image analysis was used to determine the contact angles. The averaged contact angle values from each liquid were used to calculate the surface energy of the coating using the Owens-Wendt method.[28] This analysis was performed before and after water aging to assess the stability of the coatings upon water immersion.

2.2.7.2. Pseudobarnacle adhesion: Pseudobarnacle (PB) adhesion measurements were performed using a Symyx® Automated Pull-Off Adhesion System where the force required for the removal of an epoxy-glued aluminum stud (pseudobarnacle) from the coating surface was measured.[29] The array panel on which the coating had been applied was placed on a vacuum plate which held the panel in place. A plastic template was placed over the array panel, which had three seven mm diameter holes in a line over each coating patch. The two-component epoxy adhesive (Loctite® Hysol® 1C-LV) was spread over the plastic template, leaving epoxy adhesive behind in where holes were present. The plastic template was removed and the array panels were placed into clamping jigs. In most cases, three pseudobarnacles were applied per coating, and weighted foam blocks were

placed over the studs for overnight curing. The following day, the foam blocks were removed, and the panels that were clamping jigs with panels enclosed were placed into the automated adhesion system. An automated pull-off head removed the pseudobarnacles by applying gradual force. The force at release was recorded for all three measurements and an average was calculated.

2.2.8. Assessment of siloxane-polyurethane coating fouling-release performance via biological laboratory assays

2.2.8.1. Coating pre-leaching and aging: The coatings were pre-leached and aged in a recirculating deionized water tank in which a UV sterilizer, submicron filter, and an activated charcoal filter were employed to maintain the water quality. The fouling-release performance of the siloxane-polyurethane coatings was performed following two weeks of pre-leaching in the recirculating water tank. This was done for all of the experimental coatings, including those applied to panels and deposited into 24-well plates.

2.2.8.2. C. lytica *biofilm retention:* The high-throughput assessment of bacterial biofilm retention on coatings prepared in 24-well plates has been described previously.[19 30-32] The coatings were inoculated with 1.0 ml of a 10^7 cells ml^{-1} suspension of *C. lytica* in BGM and incubated at 28°C for 24hr. Following the incubation, the BGM and planktonic growth were discarded and the plates were rinsed three times with ASW to remove unattached cells, or biofilm that was only weakly attached. The retained biofilms were dried at ambient laboratory conditions, for ~1 hr and stained with crystal violet (0.3% w/v in deionized water). The crystal violet stain was subsequently extracted from the biofilm retained on the coating

surfaces with 0.5 ml of 33% glacial acetic acid and the absorbance of the resulting eluates was measured for absorbance at 600 nm. This was repeated for a total of three replicate wells. The absorbance values were considered to be directly proportional to the amount of biofilm retained on the coating surfaces.

2.2.8.3. N. incerta *cell adhesion assay in 24-well plates:* The *N. incerta* cell adhesion assay was carried out in a similar manner to that described for *C. lytica* biofilm retention assay.[13,33,34] Coatings that were prepared in 24-well plates were inoculated with 1.0 ml of a 10^5 cells ml^{-1} suspension of *N. incerta* in F/2 and incubated at ambient laboratory conditions for 2 hr. Water jetting followed the incubation of the plates. For each coating system, four replicate wells were treated with the water-jet at 43 kPa for 10 sec while four replicate wells were not treated and served as the amount of *N. incerta* cells initially attached to the coating surfaces. 1.0 ml DMSO was immediately added to each well and the plates were incubated in darkness for 30 min. A homogeneous solution was obtained by gentle shaking and 0.2 ml of the solution was transferred to a 96-well plate for fluorescence measurements of chlorophyll using a multi-well plate spectrophotometer (excitation wavelength: 360 nm, emission wavelength: 670 nm). The percent removal was recorded as the difference in relative fluorescence units (RFU) between the coating replicates that were exposed to the water-jet and those which were not.

2.2.8.4. N. incerta *biofilm adhesion assay on drawdown array plates:* Primed array panels, coated with eight experimental coatings, and two coating patches of each of the silicone standards were aged in a circulating water tank for

four weeks in addition to the two weeks described above. Before testing began, the panels were equilibrated in artificial sea water for 2hr. Six replicate panels were placed in tanks and 1 L of *N. incerta* (cell inoculum adjusted to 0.05 at absorbance 660 nm) was added so that the panels were completely covered. The panels were left for 3hr before gently adding 9 L of ASW to the corner of each tank. The panels were then gently moved back and forth in the tank to remove non-attached cells, the pumps were turned on, and Guillard's culture medium was added to a 1:9 dilution with ASW. After two days, a brown biofilm covered the surface and individual panels were exposed to the water jet at a series of different impact pressures (64 kPa, 73 kPa, 93 kPa and 132 kPa) and percentage removal was visually assessed.

2.2.8.5. Ulva *sporeling release assay: Ulva linza* is a green macroalga that reproduces by producing large numbers of motile zoospores that rapidly settle and adhere to the substratum through the release of a glycoprotein adhesive(s).[35 36] Settled spores germinate and grow into sporelings (young plants). The removal assay quantifies the strength of attachment of sporelings to the coating. Spores of *Ulva* were released into artificial seawater at pH 8.0 and 32% and prepared for assays as described by Callow *et al.* (1997). Additional water aging for a period of two weeks was performed for the coatings prior to testing. Before the start of the assay, each well of the 24-well plates was filled with deionized water, allowed to stand for 48hr and subsequently equilibrated in artificial sea water for 2hr. A single coating type was deposited all of the 24 wells of a plate. The *Ulva* spore inoculum was adjusted to 5×10^5 spores ml^{-1}. Each well was inoculated with 1 ml of the

spore suspension and immediately placed in the dark for 2 hr. After washing, which removed unattached i.e. motile, spores, attached spores were grown for 7 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 hr.[20] After 7 days growth, the coatings were exposed to 18, 67 or 111 kPa impact pressure with a rotating water jet. One row of each 24-well plate (6 replicates) was not jetted while three rows were jetted using a different pressure for each row resulting in 6 replicates per pressure. Biomass was determined by extraction of chlorophyll as described for *Navicula*. Percentage removal was calculated from the mean chlorophyll concentration before and after water-jetting.[20]

2.2.8.6. Adult barnacle reattachment assay: An adult barnacle reattachment assay was utilized to gauge the fouling-release performance of the coatings with respect to shell fouling.[13,26,33,37,38] Adult barnacles (*Amphibalanus amphitrite (=Balanus amphitrite)*) with a basal diameter of approximately 5 mm were removed from a PDMS substrate (Silastic-T2 on glass) and placed on the coating surfaces. Nine barnacles were used for testing each coating where three barnacles were placed on three replicate coating patches of the draw down array panels. The barnacles were allowed to reattach to the coating surfaces by immersing the array panels in an ASW aquarium system for 14 days with daily feedings of brine shrimp nauplii. The reattached barnacles were dislodged from the coating surfaces using a hand held digital force gauge in accordance with ASTM D5618-94. In this regard, the force gauge was placed at the barnacle base plate, parallel to the coating surface, and pushed laterally (i.e., in shear) until it became detached from the

surface. Once detached, the area of the barnacle base plates were measured using image analysis (Sigma Scan Pro5.0) and their adhesion strengths were calculated from the removal force and the area of the barnacle base plates. The adhesion values for each coating were reported as the mean of the total number of barnacles exhibiting a measurable removal force.

2.3. Results and discussion

The goal of this study was to investigate the effect of PDMS macromer molecular weight and loading on coating properties and to evaluate the coating performance when exposed to a range of biofouling organisms. Eight experimental coatings were prepared using four different PDMS macromers, at molecular weights ranging from 1,000 to 15,000 g/mol. The percent weight loading of the PDMS based on coating solids was varied from 5% to 10% within the eight coatings. Table 2.5 summarizes the experimental coating systems discussed herein.

Table 2.5. Experimental coating composition, where PDMS macromer loading is weight % loading based on coating solids

Coating ID	PDMS Theoretical MW (g mol^{-1})	PDMS Loading
1	1,000	5%
2	1,000	10%
3	5,000	5%
4	5,000	10%
5	10,000	5%
6	10,000	10%
7	15,000	5%
8	15,000	10%

The macromers were characterized by Rapid GPC, and the results are shown in Table 2.6. The GPC results show that the macromers covered a range of molecular weights, and that molecular weights near the target values were obtained. The siloxane-polyurethane coatings prepared from the incorporation of these macromers into a polyurethane coating system show high water contact angles and low surface energies typical of siloxanes, confirming the presence of PDMS at the coating surface. These properties are retained upon water aging of the coatings for 21 days, as shown in Figure 2.1 and Figure 2.2. There is little difference in properties between coatings prepared with 5% and 10% PDMS macromer. Coatings prepared with higher molecular weight PDMS macromer showed better retention of properties upon water immersion. The coatings prepared with low molecular weight PDMS (1000 g/mol) showed lower water contact angles and higher surface energy after water immersion while coatings prepared with higher molecular weight PDMS showed little change in properties after water immersion.

Table 2.6. Rapid GPC results from the molecular weight characterization of PDMS macromers at four theoretical molecular weights, relative to polystyrene standards.

Theoretical MW ($g\ mol^{-1}$)	$\overline{M_n}$	$\overline{M_w}$	PDI
1,000	2,200	2,500	1.2
5,000	6,700	8,700	1.3
10,000	11,300	15,500	1.4
15,000	12,100	16,700	1.4

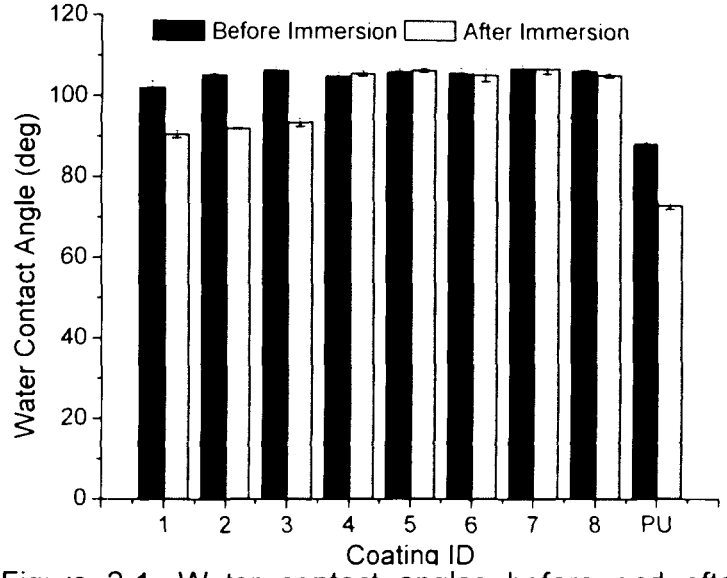


Figure 2.1. Water contact angles before and after coatings were immersed in water for 21 days. The values represent averages of 3 measurements, and the error bars show their standard deviations.

The results from the PB adhesion testing are shown in Figure 2.3. As expected, the polyurethane control coating showed high PB adhesion. The experimental coatings showed low removal forces in every case, illustrating the reduction of adhesion caused by the PDMS surface of the self-stratified coatings. There was little correlation between the PDMS loading level or PDMS molecular weight and the PB removal force as all experimental coatings showed low PB removal forces. The automated adhesion instrument lacks sensitivity in the 8-10 N adhesive force range, as the sensitivity limit of the instrument is reached. However, the data presented herein shows the potential for superior release performance from these coatings, especially compared to the polyurethane control. It also illustrates, like surface energy analysis, that the PDMS component is present at the coating surface, providing low PB removal forces. While the coatings

performed similarly in this test, the PB adhesion test is still a valuable screening tool, as it has previously been shown to correlate well with the live adult barnacle reattachment assay.[13]

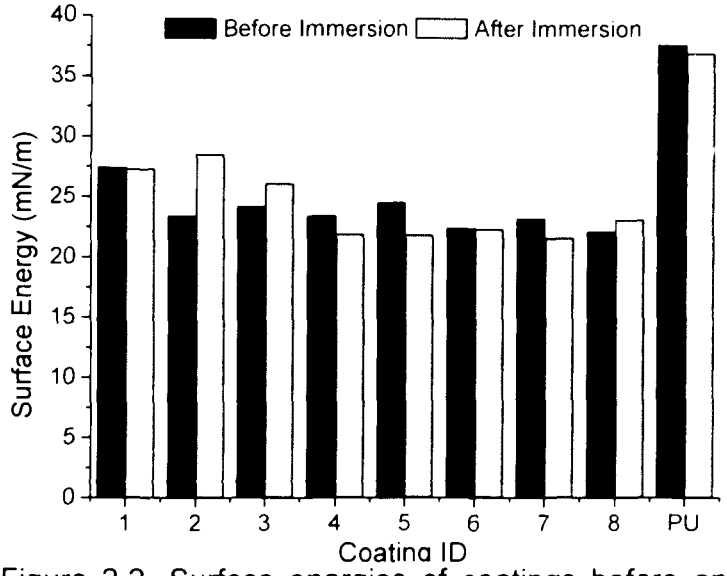


Figure 2.2. Surface energies of coatings before and after being immersed in water for 21 days. The reported values were calculated using the Owens-Wendt method from the average contact angles of three measurements using both water and methylene iodide.[28]

The biofilm retention bioassay was performed with the marine bacterium, *C. lytica*. As shown in Figure 2.4, there was a difference in biofilm retention for some of the coatings, though overall retention was low compared to both the polyurethane control and silicone standards. This can be seen in the graphical representation (Figure 2.4b), and also by a photograph taken of the coatings after the biofilm was stained with crystal violet (Figure 2.4a). In the photograph, the purple stain illustrates the presence of bacteria. For coatings prepared with low

molecular weight PDMS (1,000 g/mol), there was a substantial difference in retention where coatings prepared with 5% PDMS retained a greater amount of biofilm than the coating prepared with 10% of the same PDMS. Aside from these two compositions, however, there appeared to be little difference between the coatings, as only a very small amount of biofilm was retained.

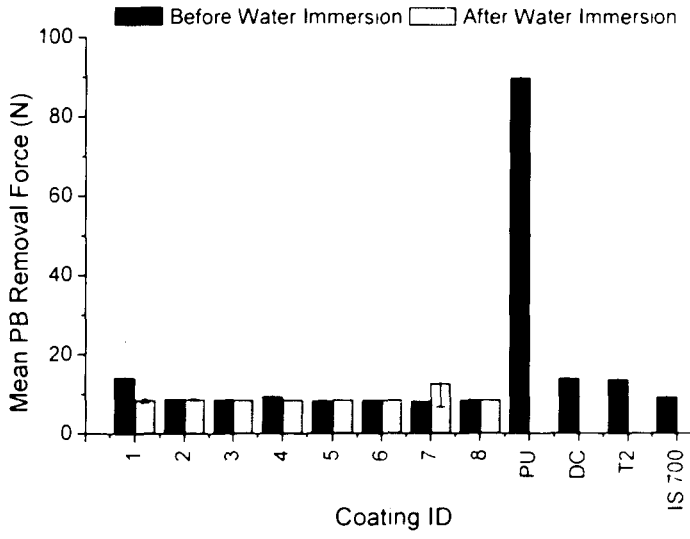


Figure 2.3. Pseudobarnacle adhesion for experimental and polyurethane coatings before and after 21 days of water immersion. The values shown are the means of at least three measurements and the error bars represent one standard deviation of the mean.

The low biofilm retention shows that the bacteria did not adhere as well to the experimental coatings compared to the control and silicone standards, even though the same quantities of bacteria were present for attachment. Bacterial cells may have been attached so weakly that they became detached upon very light rinsing. Additionally, a smaller area of the experimental coating surfaces became

covered by attached bacteria compared to the silicone standards and polyurethane control. This can be seen in Figure 2.4a as well, as a smaller portion of the coating was covered with purple-stained bacteria. The inability of cells to remain attached to the surface for quantification or to form a continuous biofilm illustrates the potential for high fouling-release performance of higher organisms.

The attachment and the removal of cells of *N. incerta* from the coating surface upon water jetting (in 24 well plates) are shown in Figures 2.5 and 2.6. In terms of cell attachment, a lower cell attachment was observed for the experimental coatings compared to the standards. The coatings with 5% PDMS loading showed higher attachment of the diatom than the same coatings with 10% PDMS loadings, in most cases. Water jetting of *N. incerta* from the coating surfaces showed the highest removal of the diatom on coatings prepared with low molecular weight PDMS (1,000 g/mol, and 10% 5,000 g/mol). However, removal from other coatings was not as high, as coatings 5, 6, and 8 showed low removal of diatoms from the surface. When coatings were analyzed as applied to primed panels, similar results were observed, as shown in Figure 2.7. Coatings prepared with low molecular weight PDMS (1,000 and 5,000 g/mol) showed the highest removal of the diatoms upon water jetting at a similar pressure to that used in the 24 well plates. Although the removal in this case was visually estimated (based on 100% initial coverage). there seemed to be little difference in performance based on PDMS loading level.

Diatoms are known to adhere strongly to silicone-based coatings,[21] so their tendency to adhere more aggressively to the coatings with higher molecular weight

PDMS is not surprising, as there could be a greater concentration of PDMS at the surface of those coatings. However, some of the coatings with low molecular weight PDMS show even greater removal of the diatoms than the more polar polyurethane control which typically shows good removal of this alga. The difference in performance correlates with the surface energy data (Figure 2.2), where a slightly higher surface energy was observed for the coatings prepared with lower molecular weight PDMS following water immersion.

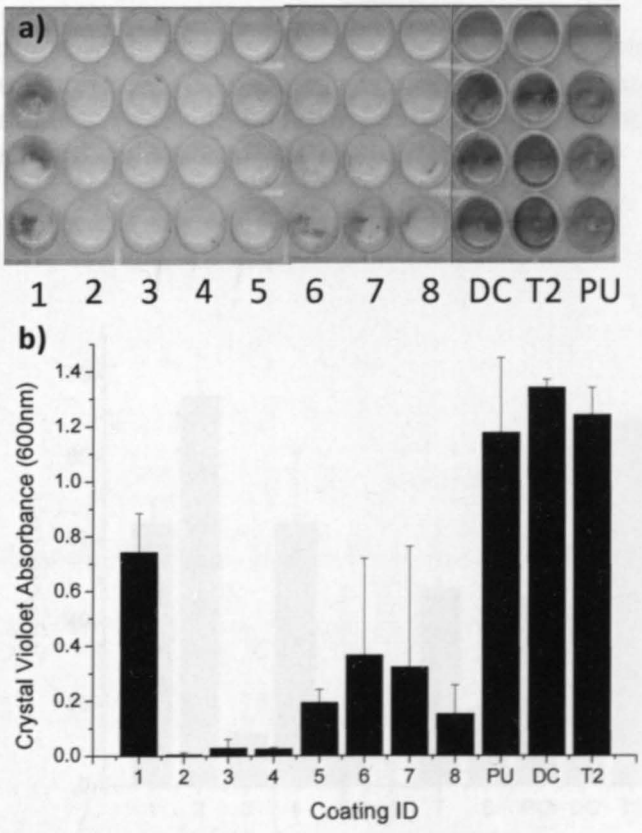


Figure 2.4. Biofilm retention of *C. lytica*. a) shows the coatings with attached biofilm after staining with crystal violet and the top wells show bare coatings. b) is a graphical representation of the attached biofilm where the values shown are the mean of three measurements and the error bars represent one standard deviation of the mean.

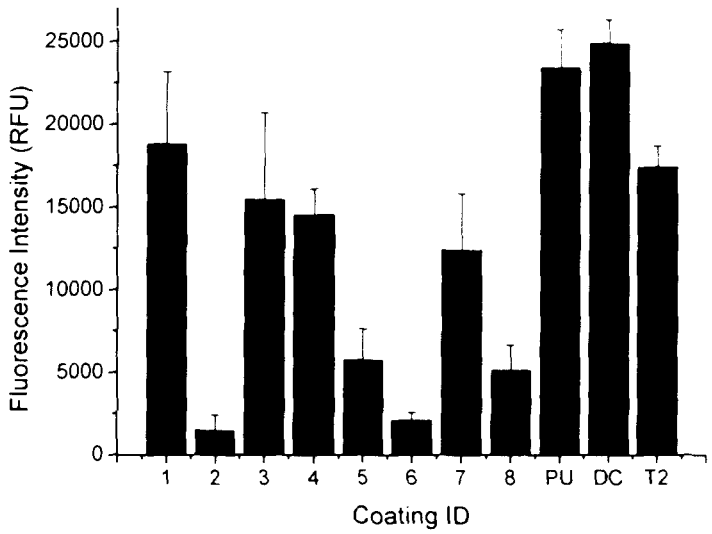


Figure 2.5. Attachment of the diatom *N. incerta* measured at. The reported values are the mean of 3 measurements and the error bars represent one standard deviation of the mean (NDSU).

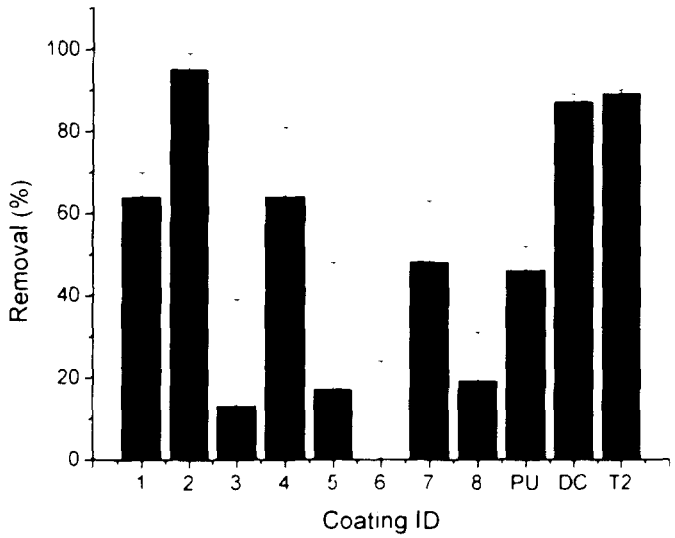


Figure 2.6. Removal of *N. incerta* upon water jetting at 43 kPa for 10 sec. The reported values are means of 3 measurements and the error bars represent one standard deviation of the mean (NDSU).

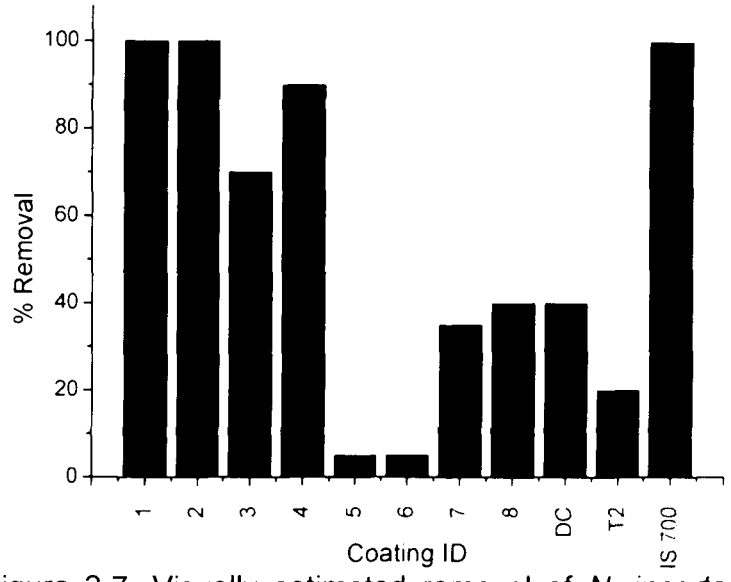


Figure 2.7. Visually estimated removal of *N. incerta* from drawdown coatings following water jetting at 64 kPa, the lowest pressure used (University of Birmingham).

The two organisms *Ulva* and *N. incerta* tend to show opposing responses to coatings, with sporelings of *Ulva* being more easily removed from hydrophobic coatings than hydrophilic coatings.[39 40] The removal of sporelings from the surface of the coatings upon water jetting at several pressures is shown in Figure 2.8, where the coatings are compared to silicone standards and a polyurethane control (for this experiment, Coating 1 was not included in analysis, as there was insufficient PDMS macromer to formulate the coating). There is greater removal of sporelings from coatings containing higher molecular weights of PDMS. Removal is lowest from coatings 2 and 3 containing 1,000 and 5,000 g/mol MW PDMS respectively, and these coatings had the lowest contact angles after immersion in water (Figure 2.1). The data correspond with those for the *C. lytica* biofilm retention assay, there being little difference in performance whether 5% or 10%

PDMS is added to the coatings, where 5% PDMS provides a similar result as the inclusion of 10% PDMS. The performance of many of the coatings (5, 6, 7, and 8) was comparable to that of the silicone standards at all impact pressures, illustrating their potential as fouling-release coatings.

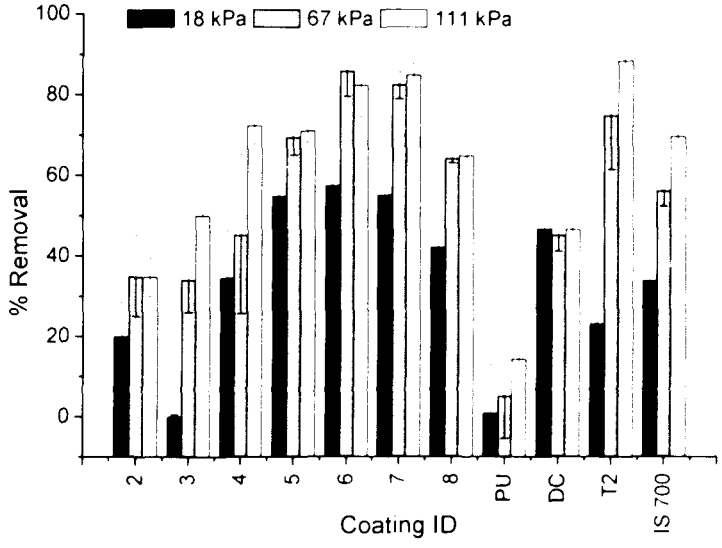


Figure 2.8. Removal of *Ulva* sporelings upon water jetting at 18, 67, and 111 kPa; the values shown are the mean calculated from 6 replicates and the error bars represent the 95% confidence intervals derived from arcsine transformed data.

The adhesion force to remove reattached (14 days) adult barnacles on the coating surfaces are shown in Figure 2.9. These coatings were pre-leached for 14 days prior to barnacle reattachment. In this assay, as was observed in the *Ulva* sporeling removal assay, the coatings prepared with lower molecular weight PDMS showed the poorest performance, with the highest adhesion forces observed for coatings 1 and 2. Coatings 4, 5, 6, 7, and 8 showed very low removal forces while coating 3 showed a comparatively moderate average removal force. However,

even coatings 1 and 2 which had the lowest highest removal force exhibited performance comparable to the DC and T2 standards that were tested. It should be noted, however, that the coatings with low removal force (4, 5, 6, 7, and 8) also had small standard deviations, showing their consistency in performance. Furthermore, the adhesion force of reattached barnacles was similar to the value obtained for Intersleek® 700.

The same panels assessed for barnacle reattachment in Figure 2.9 were immersed in the recirculating water tank (pre-leached) for an additional 35 days. A new set of barnacles were reattached to the coatings for 14 days, and barnacle adhesion was measured again. The data from this set of barnacles is shown in Figure 2.10 where nine measurements were attempted, and the data labels represent the number of barnacle which broke during testing and for which data was not included. As shown, the reattached barnacles adhered more strongly to the coatings after extending the pre-leaching period. While samples prepared with low molecular weight PDMS showed broken barnacles, the coatings prepared with the higher molecular weight PDMS macromers showed release of all nine barnacles. Even though the removal forces are higher, the barnacles are still being released from the coating surface. It is possible that the performance of the coatings has changed after additional water aging, but conclusions cannot be drawn based on this limited data alone, and further assessment should be conducted. Chapter 3 of this dissertation details an experiment where extended water aging was carried out with these same coatings, and their fouling-release performance was assessed.

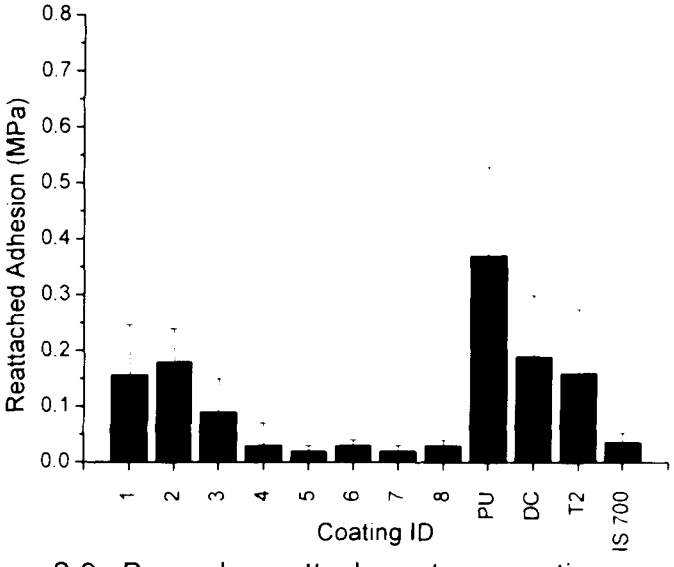


Figure 2.9. Barnacle reattachment on coatings pre-leached for 14 days. The values are means of nine measurements. Error bars represent one standard deviation of the mean.

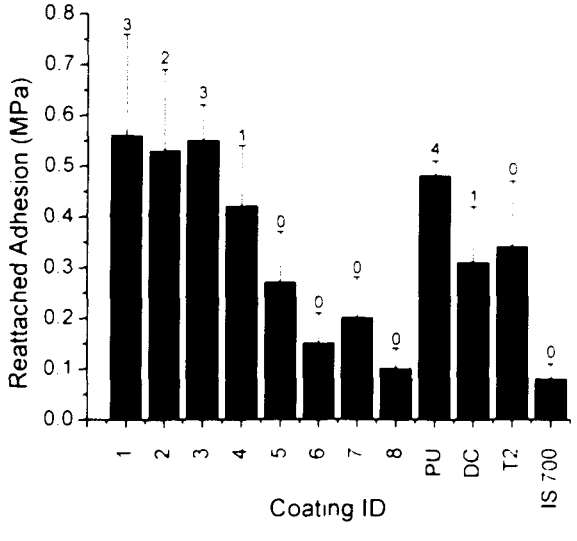


Figure 2.10. Barnacle reattachment after 49 days of pre-leaching. The values are the means of nine attempted measurements. where the data labels show the number of broken barnacles (data not included). Error bars represent one standard deviation of the mean.

2.4. Summary and conclusions

As a preliminary study, this set of experiments shows the applicability of siloxane-polyurethane fouling release coatings based on PDMS macromers. Most coatings are low in surface energy before and after water immersion, showing that they are stable upon water immersion. The PB removal force was low for all of the coatings and in the bioassays, some of the coatings showed release performance that was comparable to or superior to that of standard siloxane coatings that were tested. All of the coatings showed relatively low *C. lytica* biofilm retention where coatings 2, 3, 4, 5, and 8 showed the lowest retention. In the *N. incerta* 24 well plate assay, coatings 1 and 2 with low molecular weight PDMS showed the greatest removal of the diatom upon water jetting. Also observed was an increase in diatom attachment to the coating surface when 5% of PDMS was incorporated than when 10% was included. A similar study performed on drawdown coatings showed a similar trend in diatom removal, where coatings 1 and 2 showed the highest removal with coatings 3 and 4 also showing high removal and coatings 5, 6, 7, and 8 retaining more biofilm upon water jetting. The *Ulva* sporeling removal assay showed the opposite result, where the coating release performance improved as the PDMS molecular weight increased, for almost every coating at every water jetting pressure. Many of the coatings performed comparably to fouling release standards used in the study, including the commercial fouling-release coating, Intersleek©.

In general, the results from this study are promising, as the siloxane-polyurethane coatings developed herein have exhibited performance comparable

to fouling release standards, and even commercially available fouling release paints. The reported results show the potential of these systems to serve as fouling release coatings that are tough and durable, and provide good release performance. Laboratory screening performed within provides insight into the fouling release performance of a film, but further conclusions will necessitate ocean testing to provide a true measure of these coatings' performance as fouling release systems.

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CHAPTER 3. EXTENDED WATER AGING OF SILOXANE-POLYURETHANE FOULING-RELEASE COATINGS BASED ON PDMS MACROMERS

3.1. Introduction

Marine biofouling is the accumulation of organisms onto surfaces that are placed in sea waters[1] and is estimated to cost the US Navy $1 billion annually.[2] Fouling of marine vessels increases the roughness of the underwater surface and increases friction which leads to reduced maneuverability and efficiency.[1] It has been documented that even a light slime layer can increase the fuel consumption of a vessel.[3] While overall fouling has been said to increase fuel consumption by up to 40%[4], a light slime layer can cause a 25% increase alone.[5] Environmental factors such as increased pollution and transport of organisms between ecosystems are additional issues that arise from the accumulation of fouling onto marine vessels.[6]

Fouling-release (FR) coatings are one way in which coatings are used to combat biofouling on marine vessels. Unlike antifouling (AF) coatings which prevent the fouling of ships by the inclusion of toxic active ingredients, FR coatings allow for the weak adhesion of organisms and facilitate their easy removal.[7] An alternative to traditional FR coatings based on silicone elastomers, siloxane-polyurethane coatings are promising due to the inherent toughness of polyurethanes and the low surface energy siloxane surface which they provide.[8] Siloxane-polyurethane FR coatings have been previously described, and have shown promising FR performance comparable to commercial FR coatings.[9]

In this chapter, the coatings prepared and tested in Chapter 2 were prepared again, to explore the effect of extended underwater aging on the coating properties and FR performance. This was done because continued analysis of the systems in Chapter 2 showed a reduction in performance when the coatings were exposed to longer water aging. Therefore, further experimentation was required to understand how the coating properties and performance were affected by extended water aging. This is important, as vessel coatings are exposed to continual water aging for the lifetime of the coating and performance depletion during the coating lifetime is cause for concern.

Four aminopropyl terminated poly(dimethylsiloxane) (PDMS) macromers (APT-PDMS-M) were prepared at varying molecular weights (1,000, 5,000, 10,000, and 15,000 g mol^{-1}) using living anionic polymerization of cyclic siloxane monomers.[10,11] Eight experimental coatings were prepared using the four APT-PDMS-M at two binder mass concentrations (5 and 10%). Siloxane-polyurethane coatings were composed of APT-PDMS-M, a polycaprolactone polyol, and isophorone diisocyanate trimer. Replicates of each coating were aged for each 1, 4, and 8 week periods. Following aging, the coatings were characterized for water contact angle (WCA), surface energy (SE), pseudobarnacle (PB) adhesion, *Celulophaga lytica* (*C. lytica*) biofilm retention, *Navicula incerta* (*N. incerta*) attachment and removal, *Halomonas pacifica* (*H. pacifica*) biofilm retention and removal, and adult barnacle reattachment.

3.2. Experimental

3.2.1. Materials

Hexamethylcyclotrisiloxane (D_3) and dimethylchlorosilane (DMCS) were received from Gelest, Inc. Lithium trimethylsilanolate (LTMS) solution (1.0 M in dichloromethane), chloroplatinic acid hexahydrate, allylamine, inhibitor-free tetrahydrofuran (THF), activated carbon powder, dibutyltin diacetate (DBTDAc), and acetyl acetone (2,4-pentanedione, PD) were received from Sigma-Aldrich. Tolonate IDT 70B (isophorone diisocyanate trimer (IDT), 70% in butyl acetate) was received from Rhodia. Methyl amyl ketone (MAK) was supplied by Eastman Chemical. Tone polyol 0305 (polycaprolactone triol, PCL) was received from Dow Chemical. Intergard 264, Intersleek 700 (IS 700), and Intersleek 900 (IS 900) were received from International Paint and prepared according to the manufacturer's specifications. Silastic T2 and DC 3140 were received from Dow Corning and thinned with methyl isobutyl ketone. A polyurethane coating (PU) was prepared from PCL and IDT as a control coating (without PDMS).

C. lytica was provided by Dr. Michael Hadfield of the University of Hawaii Kewalo Marine Laboratory and *N. incerta* was provided by Dr. Maureen Callow the University of Birmingham, UK. Collection of *U. linza* was performed at Llantwit Major, Glamorgan, Wales, UK (52° 23' N; 3° 30' W). Dissolution of sea salts (38.5 g) received from Sigma-Aldrich in 1 l of deionized water yielded artificial sea water (ASW). Bacterial growth medium (BGM) was prepared by adding yeast extract (0.1 g) and peptone (0.5 g) to 1 l of ASW. Growth medium for algae (F/2) was prepared by the addition of nutrients to ASW to yield Guillard's F/2 medium. Sterilization of

ASW, BGM, and F/2 was carried out by vacuum cap filtration (0.2 μm). Crystal violet (CV) powder and dimethyl sulfoxide (DMSO) were received from VWR International and used without further purification.

3.2.2. PDMS macromer polymerization

As described previously, PDMS macromers with monohydride functionality (HT-PDMS-M) were prepared by the anionic ring opening polymerization of D_3, initiated by LTMS.[9] The polymerization was carried out in a 50% solution in THF at room temperature with magnetic stirring in a nitrogen (N_2) environment. Monomer (D_3) was dissolved in inhibitor-free THF and measured into a N_2 purged and sealed round bottom flask (RBF). The solution was degassed for 15 min and the initiator solution was introduced with stirring at room temperature. Polymerization was allowed to proceed at room temperature for 2 hr with magnetic stirring. Termination of the living chain ends was carried out by the addition of DMCS (100% molar excess) at room temperature, while maintaining the N_2 environment. Magnetic stirring was continued overnight to ensure that all polymer chain ends were terminated. The reagents used in the preparation of monohydride terminated PDMS macromers (HT-PDMS-M) are outlined in Table 3.1.

Table 3.1. Reagents used in the polymerization of hydride terminated PDMS macromers where the ratio of D_3 to LTMS determined the theoretical molecular weight of the PDMS macromers.

Theoretical MW ($g\ mol^{-1}$)	D_3			LTMS			DMCS	
	D_3 Soln (g)	Mass (g)	mmol	LTMS Soln (g)	Mass (g)	mmol	Mass (g)	mmol
1,000	72.4	36.19	163	51.9	3.9	41	10.0	105
5,000	98.4	49.2	221	25.6	1.9	20	5.0	53
10,000	99.1	49.6	223	12.6	1.0	10	2.5	26
15,000	99.4	49.7	223	8.5	0.6	7	1.7	18

3.2.3. PDMS macromer functionalization

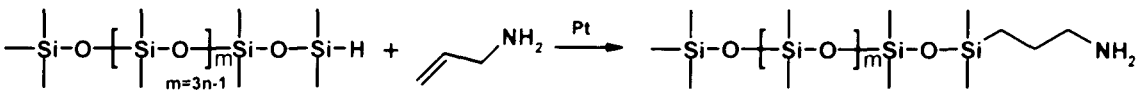
The functionalization reactions of HT-PDMS-M were carried out by the hydrosilylation of the macromer with allylamine in the presence of chloroplatinic acid hexahydrate as a catalyst. Scheme 3.1 shows the synthetic procedure for the functionalization of the PDMS macromers. Hydrosilylation was carried out in a nitrogen environment inside a RBF, sealed with a rubber septum affixed with needles to allow venting. The hydrosilylation was carried out at 90°C until the disappearance of the silicon hydride peak (4.7 ppm) in proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) was observed. The functionalization reactions were carried out in segments of 24-25 hr, and the NMR spectra were checked following each segment. Additional reagents were also added between reaction segments to help push the hydrosilylation reactions to completion. Table 3.2 outlines the total materials and reaction times used in the hydrosilylation reactions.

Following hydrosilylation, all of the reaction mixtures had turned dark brown (nearly black) in color. To remove color, extraction in methanol was performed. After isolating the product following extraction, the polymers were stirred overnight in toluene in the presence of activated carbon powder. The solutions were centrifuged and passed through an alumina column to remove the activated carbon powder and additional color. Rotary evaporation was used to isolate the polymers from toluene.

3.2.4. Characterization of PDMS macromers

3.2.4.1. Symyx® Rapid GPC: High-throughput gel permeation spectroscopy (GPC) was performed to determine the molecular weight of the PDMS macromers.

relative to polystyrene standards using a Symyx® Rapid GPC. The characterization was performed using solutions prepared at 2 mg ml^{-1} in stabilized THF. An evaporative light scattering detector (PL-ELS 1000), 2 x PLgel mixed-B columns (10μm particle size), and a flow rate of 2.0 ml min^{-1} were used to perform the analysis.



HT-PDMS-M APT-PDMS-M

Scheme 3.1. Functionalization of HT-PDMS-M through hydrosilylation with allylamine to yield APT-PDMS-M.

Table 3.2. Total reaction times and reagents used in the functionalization of PDMS macromers through hydrosilylation of HT-PDMS-M with allylamine to yield APT-PDMS-M.

Theoretical MW (g mol^{-1})	HT-PDMS-M		Allylamine		Total Catalyst (mmol)	Total Reaction Time (hr)
	Mass (g)	Approximate mmol	Mass (g)	mmol		
1,000	11.1	11.1	10.2	179	0.11	94
5,000	75.1	15.0	11.2	196	0.17	74
10,000	68.7	6.9	7.2	127	0.17	74
15,000	75.2	5.0	5.3	92	0.17	74

3.2.4.2. NMR Spectroscopy: Proton NMR (^{1}H-NMR) spectroscopy was performed using a Jeol 400 MHz spectrometer fixed with an autosampler. Solutions were prepared at 25 mg ml^{-1} in deuterated chloroform. Sixteen scans were performed with a 0.3 sec delay time.

3.2.5. Siloxane-polyurethane coating formulation

Siloxane-polyurethane coatings were formulated using the APT-PDMS-Ms, where the polyurethane bulk was composed of PCL (90% in MAK) and IDT (70% in butyl acetate). PD was used as a pot-life extender (10% weight based on formulation), DBTDAc as a catalyst (1% in MAK), and MAK and butyl acetate were present as solvents. The coatings were formulated so that a ratio of 1.1 to 1 of isocyanate to amine and hydroxyl functional groups was obtained. The amounts of reagents used to formulate approximately 15 g of coating formulation are outlined in Table 3.3. To prepare the coatings, APT-PDMS and IDT were first pre-mixed for 1.5 hr to allow each primary amine to react with an isocyanate group without competition. The addition of PCL solution, DBTDAc solution, and PD followed, respectively.

Table 3.3. Formulation recipes for the preparation of siloxane-polyurethane coatings based on PDMS macromers, formulated with APT-PDMS-M, IDT, PCL, DBTDAc, and PD.

Coating ID	APT-PDMS-M (g)	Tolonate IDT 70B (g)	90% PCL in MAK (g)	1% DBTDAc in MAK (g)	PD (g)
1	0.50	9.27	3.35	0.15	1.33
2	1.00	8.87	3.10	0.15	1.31
3	0.50	9.20	3.40	0.15	1.32
4	1.00	8.73	3.21	0.15	1.31
5	0.50	9.19	3.41	0.15	1.32
6	1.00	8.72	3.22	0.15	1.31
7	0.50	9.19	3.41	0.15	1.32
8	1.00	8.71	3.22	0.15	1.31

3.2.6. Siloxane-polyurethane coating preparation and curing

The coatings used in barnacle reattachment were prepared on aluminum Q-panels (4 x 8 in., 0.6 mm thick, type A, alloy 3003 H14, obtained from Q-lab) which had been previously primed with Intergard 264 (70-80 μm) via air-assisted spray application. The coatings used for surface energy and pseudobarnacle adhesion were applied to the same panels, without primer, which had been cleaned with acetone and xylenes. Drawdowns of the coatings onto the previously described substrates were prepared using a drawdown bar with an 8 mil gap.

Coatings for laboratory assays of bacteria and algae were dispensed (250 μl) into the bases of 24-well polystyrene plates which contained aluminum disks primed with Intergard 264 (disks had been punched from primed 4 x 8 in. Q-panels). The siloxane-polyurethane coatings (on panels and in plates) were ambient cured overnight and oven cured at 80°C for 45 min the following day. Standard silicone coatings and commercial fouling-release coatings were also prepared in 24-well plates for biological analysis. These systems were ambient cured for 24 hr (7 days for DC 3140) under the same ambient conditions as the siloxane-polyurethane coatings. Table 3.4 summarizes the compositions of the coatings used in this study.

3.2.7. Characterization of siloxane-polyurethane coating physical properties

3.2.7.1. Contact angle and surface energy: Contact angle and surface energy (SE) measurements were carried out using a Symyx® Coatings Surface Energy System with First Ten Angstroms software. Three contact angles of water and methylene iodide were measured on the coating surfaces. A photograph was

taken with a CCD camera, and automated image analysis was used to measure the wetting angle. The mean contact angles were used to calculate the surface energy of the coatings using the Owens-Wendt method.[12] Contact angle and surface energy measurements were made before and after each 1, 4, and 8 weeks of water aging.

Table 3.4 Dry coating compositions of siloxane-polyurethane coatings formulated using APT-PDMS-M. As shown, eight experimental coatings were examined, where the molecular weight and concentration of APT-PDMS-M in the coatings were varied.

	Weight % of solids				
Coating ID	APT-PDMS-M	IDT	TPCL	Total Solids (%)	DBTDAc (based on solids)
1	5%	65%	30%	69%	0.015%
2	10%	62%	28%	69%	0.015%
3	5%	64%	31%	69%	0.015%
4	10%	61%	29%	69%	0.015%
5	5%	64%	31%	69%	0.015%
6	10%	61%	29%	69%	0.015%
7	5%	64%	31%	69%	0.015%
8	10%	61%	29%	69%	0.015%

3.2.7.2. Pseudobarnacle adhesion: Pseudobarnacle (PB) adhesion measurements were performed using a Symyx® Automated Pull-Off Adhesion System where the force required to remove an epoxy-glued metal stud from a coating surface was determined.[13] The coated panels (2 at a time) were placed on a vacuum plate which held them in place. A plastic template with 24 patches of three 7 mm diameter holes was used to cover the panels. A two-component epoxy adhesive (Loctite® Hysol® 1C-LV) was spread over the plastic template, depositing adhesive onto the panels in designated areas. The plastic template was

removed and the panels were placed into clamping jigs where the PBs were applied. Weighted foam blocks were placed over the studs for overnight curing. The following day, the foam blocks were removed, and the clamping jigs (panels enclosed) were placed into the automated adhesion system. An automated pull-off head removed the PBs by applying gradual force. The force at release was recorded and the mean and standard deviations were calculated.

3.2.8. Assessment of siloxane-polyurethane fouling-release performance via biological laboratory assays

3.2.8.1. Water aging of coatings: The coatings were aged in a recirculating deionized water tank affixed with a UV sterilizer, submicron filter, and an activated charcoal filter. The coatings were all immersed on the same date, and were removed in batches after the designated aging time had been reached so that three different aging times of 1, 4, and 8 weeks were achieved.

3.2.8.2. Leachate toxicity: After water aging, or pre-leaching (PL), was performed, the coatings were analyzed for leachate toxicity. Extractions from each coating were performed by adding ASW and nutrients to wells of microtiter plates containing coating samples. Growth of bacteria in this environment was monitored after 24 hr, by staining with CV stain. The CV was then extracted and quantified by absorbance measurements at 600 nm. Comparison with standard coatings and negative growth controls was performed to determine that the coatings did not contain toxic leachates and biological analysis could be continued.

3.2.8.3. C. lytica *biofilm retention:* High-throughput assessment of bacterial biofilm retention on coatings prepared in 24-well plates was performed to

determine the ability of bacterial biofilm to grow on the surface of the coatings.[14-17] The wells of coated microtiter plates were inoculated with 1.0 ml of *C. lytica* suspension (10^7 cells ml^{-1}) in BGM. The plates were incubated at 28°C for 24 hr. The growth media and planktonic growth were discarded after incubation was complete and the coatings were triple rinsed with ASW to remove unattached or weakly adhered bacteria. The retained biofilms were dried for 1h under ambient conditions, and stained with CV (0.3% w/v in deionized water). Extraction of CV from the biofilm was performed with 0.5 ml of 33% glacial acetic acid and the resulting eluates were measured for absorbance at 600 nm. A total of three replicate wells were measured. The absorbance values were considered to be directly proportional to the amount of biofilm retained on the coating surfaces.

3.2.8.4. H. pacifica *biofilm retention and removal:* Biofilm retention of *H. pacifica* was performed in the same way as for *C. lytica*. The wells of coated microtiter plates were inoculated with 1.0 ml of 10% *H. pacifica* suspension (10^8 cells ml^{-1}) in BGM. The plates were incubated at 28°C for 24 hr to allow the bacterial cells to grow and attach to the coating surfaces. The growth medium and planktonic growth were discarded after incubation. The coatings were triple rinsed with ASW to remove unattached or weakly attached cells. Eight replicate wells were prepared for each coating system and each water aging period. Four wells were left untreated and four wells were water jetted for 5 sec at each 10 psi to remove the bacteria from the coating surface. The retained biofilms of both the untreated and water jetted coatings were dried for 1h under ambient conditions. and stained with CV (0.3% w/v in deionized water). Extraction of CV from the

biofilm was performed with 0.5 ml of 33% glacial acetic acid and the resulting eluates were measured for absorbance at 600 nm. A total of three replicate wells were measured. The absorbance values were considered to be directly proportional to the amount of biofilm retained on the coating surfaces. The percent removal was determined as the difference between the amount of untreated biofilm and water jetted biofilm. A high removal upon water jetting was indicative of good fouling-release performance where the bacteria were easily removed from the coating surface.

3.2.8.5. N. incerta *attachment and removal:* The *N. incerta* cell adhesion assay was carried out in a similar manner to that described for the bacterial biofilm retention and removal assays.[9,18,19] Coatings prepared in 24-well plates were inoculated with 1.0 ml of a suspension of *N. incerta* (10^5 cells ml^{-1}) in F/2. The plates were incubated for 2 hr under ambient conditions. Following incubation, the plates were treated with water jetting. Eight replicate wells were prepared for each coating system. Four replicates were water jetted at 10 psi for 10 sec and four replicates were left untreated to be measured as the cells initially attached to the coatings. The plates were incubated in darkness for 30 min with one milliliter of DMSO in each well. Gentle agitation yielded a homogeneous solution of which 0.2 ml was transferred to a 96-well plate for fluorescence measurements of chlorophyll using a multi-well plate spectrophotometer (excitation wavelength: 360 nm, emission wavelength: 670 nm). The percent removal was recorded as the difference in relative fluorescence units (RFU) between the coating replicates that were exposed to the water jet and those left unexposed.

3.2.8.6. Barnacle reattachment: An adult barnacle reattachment assay was utilized to gauge the fouling-release performance of the coatings with respect to shell fouling.[20-22] Adult barnacles (*Amphibalanus amphitrite*) with a basal diameter of approximately 5 mm were removed from a PDMS substrate and placed on the coating surfaces. Nine barnacles were used for testing each coating. The barnacles were reattached to the coating surfaces in an ASW aquarium system for 14 days with daily feedings of brine shrimp nauplii. The reattached barnacles were dislodged from the coating surfaces using a hand held digital force gauge in accordance with ASTM D5618-94. The force gauge was placed at the barnacle base plate, and pushed laterally (in shear) until the barnacle became detached from the surface. Once detached, the areas of the barnacle base plates were measured using image analysis (Sigma Scan Pro5.0) and their adhesion strengths were calculated from the removal forces and the areas of base plates. The adhesion values for each coating were reported as the mean of the total number of barnacles exhibiting a measurable removal force.

3.3. Results and discussion

The results from the characterization of the PDMS macromer molecular weights by Rapid GPC, relative to polystyrene standards are shown in Table 3.5. The molecular weights measured by GPC were similar to the target molecular weights, and a narrow polydispersity index (PDI) was achieved. Therefore, the living anionic polymerization conducted herein was effective in controlling the molecular weight of the polymers by varying the initiator to monomer ratio.

Table 3.5. Rapid GPC data for the PDMS macromers, where the analysis was performed prior to Functionalization and is relative to polystyrene standards

Theoretical MW (g mol^{-1})	$\overline{M_n}$	$\overline{M_w}$	PDI
1,000	1,700	1,900	1.1
5,000	5,700	6,500	1.1
10,000	11,200	12,800	1.1
15,000	15,100	17,200	1.1

The functionalization of the PDMS macromers was determined to be complete by the disappearance of the silicone hydride peak in 1H-NMR at 4.7 ppm. The disappearance of this peak in the NMR spectra illustrated that all of the silicon hydride bonds had been converted to silicon carbon bonds and the functionalization of the HT-PDMS-M to APT-PDMS-M was complete.

The water contact angle (WCA) measured on the surface of the coatings before and after water aging are shown in Figure 3.1. In general, the WCA on all of the coatings were high before and after water aging. However, a reduction in WCA observed following water aging in most cases while the values still remained high (90-100°). A reduction in SE was also observed for these coatings, and the SE of the coatings before and after water aging are shown in Figure 3.2. Generally, a reduction in WCA indicates an increase in hydrophilicity which usually translates to a rise in SE. The SE of the coatings decreased to near 22 mN m^{-1} following water aging, which is the SE of silicone materials. However, because the WCA had also dropped, during water aging, it is possible that these results are not due to silicone at the coating surface. These coatings were aged in the water bath alongside other coatings of miscellaneous composition. The decomposition of coatings inside the water tank could have led to the accumulation of material on the surface of our

experimental coatings. Additionally, slime had collected on the coatings during water aging and the biofilm was removed by soft sponging prior to coating analysis. One of these factors, or their combination could have led to these unexpected results.

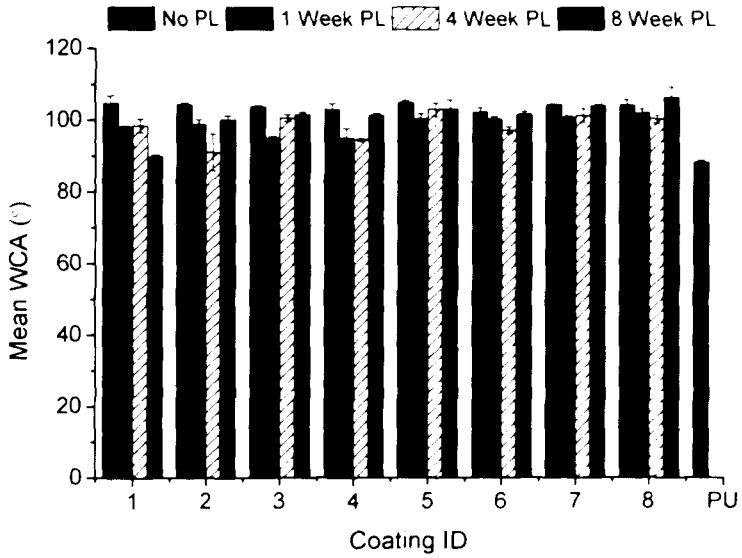


Figure 3.1. WCA measured on the surface of the coatings before and after water aging. The data points represent the mean of three measurements and the error bars represent one standard deviation of the mean.

The PB adhesion removal values for the coatings are shown in Figure 3.3. All of the experimental coatings showed low PB removal after water aging at 1, 4, and 8 weeks. The PB removal forces for these coatings were in all the range of the commercial fouling-release coatings as well, near 8-10 N while the PB removal from a pure polyurethane that did not contain PDMS was much higher, near 90 N. While this analysis doesn't involve the removal of a live organism, it does show

that the coatings maintained release performance following up to 8 weeks of water aging.

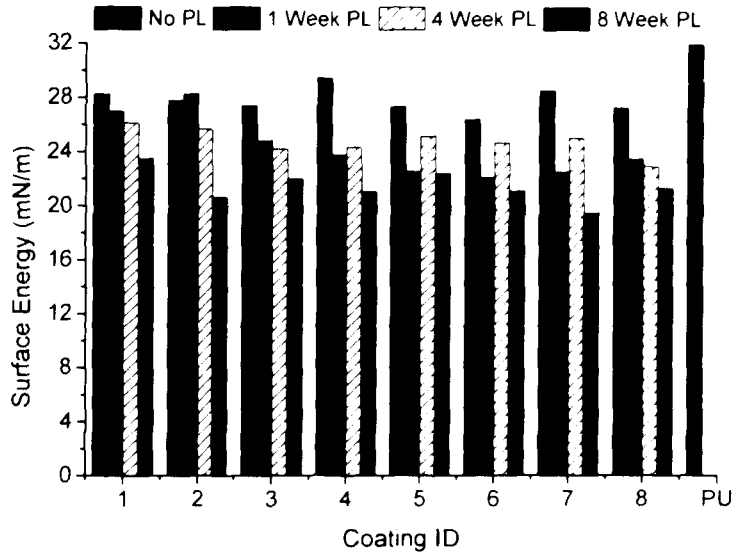


Figure 3.2. SE of the cured films before and after water aging where the values were calculated based on the Owens-Wendt method using the means of three contact angle measurements of each water and methylene iodide.[12]

The results from the *C. lytica* biofilm retention assay are shown in Figures 3.4 and 3.5. Figure 3.4 is a graphical representation of the absorbance values observed when CV was extracted from the biofilm that was retained on the coating surfaces. In this assay, similar biofilm retention was observed for the coatings at all lengths of water aging. However, there was slight variation between coating compositions, where those prepared with higher molecular weight PDMS showed reduced biofiom retention compared to those prepared with lower molecular weight PDMS. This same trend is shown in Figure 3.5, a pictoral representation of the *C. lytica* biofilm retention where the presence of purple stain indicates biofilm

retention. Coatings 5, 6, 7, and 8 show reduced biofilm retention on the coating surface for all lengths of water aging. Similar bacterial biofilm retention to IS 700 was observed on coatings 1, 2, and 3 prepared with low molecular weight PDMS as. A slightly reduced biofilm retention compared to the same commercial coating was observed for coatings 4, 5, 6, 7, and 8.

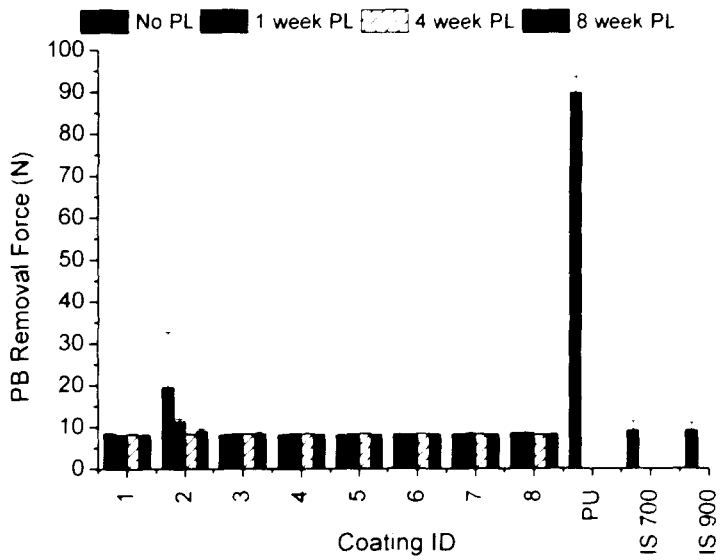


Figure 3.3. PB adhesion measured on the coating surfaces where the data points are means of three measurements in most cases, and the error bars represent one standard deviation of the mean.

The CV absorbance values observed for biofilm retention of *H. pacifica* on the coating surfaces are shown in Figure 3.6. In this case, similar biofilm retention was observed for most of the coatings and water aging times. However, coatings 4, 5, 6, 7, and 8 showed higher biofilm retention on the coatings aged for 8 weeks compared to the same coatings aged for only 1 and 4 weeks. IS 900 showed high *H. pacifica* biofilm retention after only 1 week of water aging, but showed much

lower biofilm retention after 4 and 8 weeks of water immersion. These measurements were in the range of most of the experimental coatings for all water aging times.

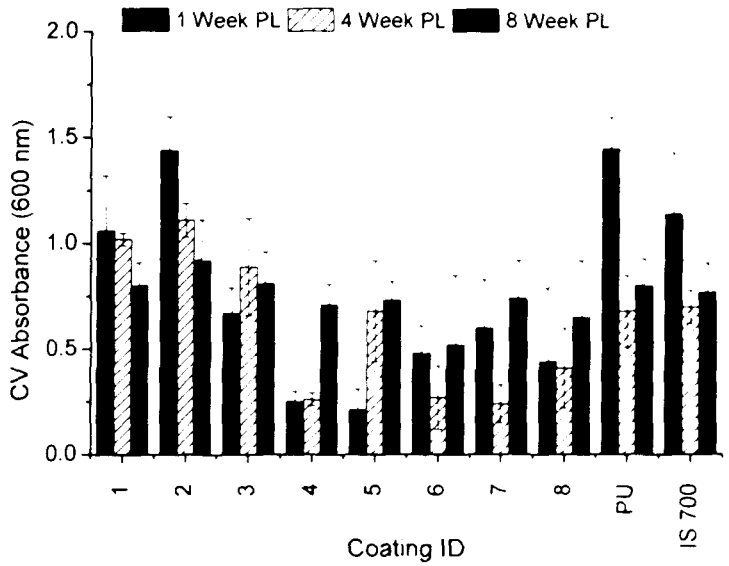


Figure 3.4. Biofilm retention of *C. lytica* where the data points are the means of three measurements and the error bars represent one standard deviation of the mean.

The removal of *H. pacifica* from the coating surfaces after water jetting at 10 psi for 5 sec is shown in Figure 3.7. Most of the coatings showed moderate (40-70%) removal of *H. pacifica* after 1 and 4 weeks of aging. The removal of *H. pacifica* from many of the coatings decreased substantially after 8 weeks of water aging. However, coatings 2 and 4 still showed levels of removal near 60% that were comparable to IS 700 and IS 900 and the PU control after 8 weeks of water aging. Even though the coatings discussed herein show performance comparable to the commercial FR coatings (especially after 1 and 4 weeks of aging), the FR

performance of the experimental coatings showed a lot of variability with water aging in comparison with the commercial coatings and PU control.

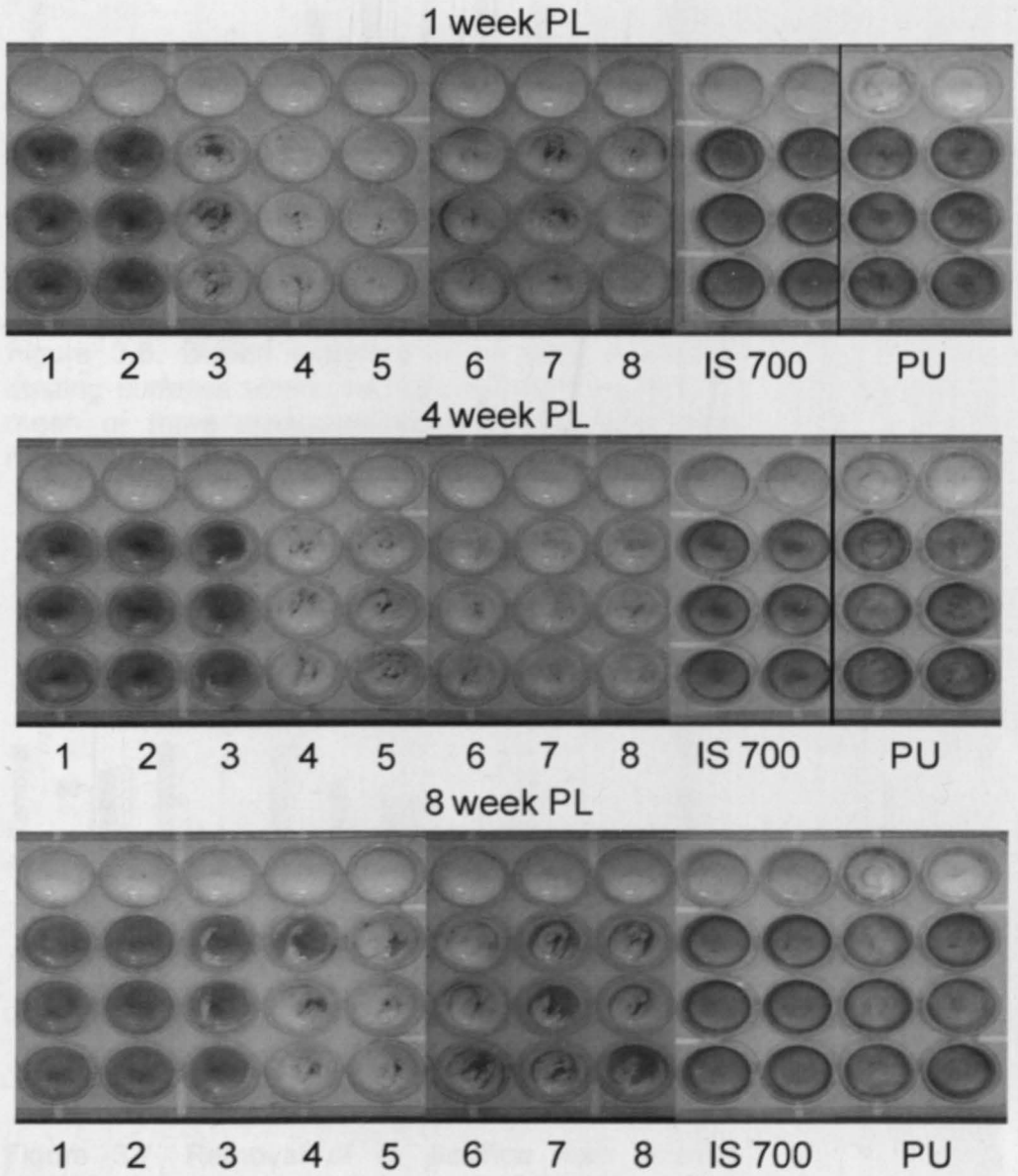


Figure 3.5. *C. lytica* biofilm retention where the presence of CV indicates retained biofilm.

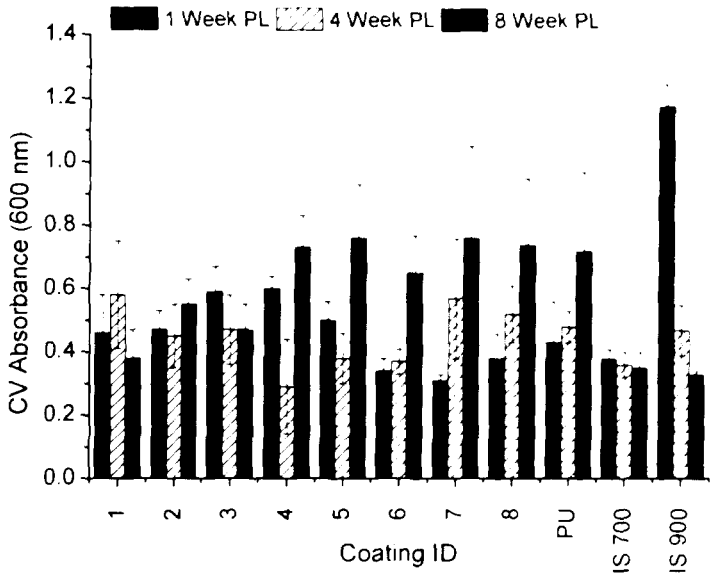


Figure 3.6. Biofilm retention of *H. pacifica* on the coating surfaces where the data points represent the mean of three measurements and the error bars represent one standard deviation of the mean.

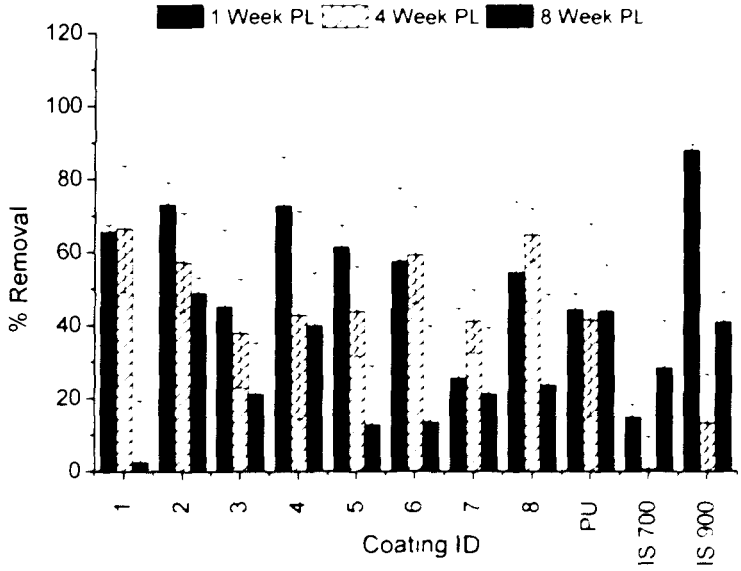


Figure 3.7. Removal of *H. pacifica* from coating surfaces following water jetting at 10 psi for 5 sec. The data represent the mean of three measurements and the error bars represent one standard deviation of the mean.

The attachment of *N. incerta* to the coating surfaces is shown in Figure 3.8. The coatings with the 1,000 g/mol PDMS macromer (coatings 1 and 2) showed a reduction in *N. incerta* attachment as water aging time was increased while all other coatings (coatings 3, 4, 5, 6, 7, and 8) showed increased *N. incerta* attachment with increased aging times. In general, however, the experimental, commercial FR standards and PU control coatings all showed some variability of *N. incerta* attachment with water aging, and similar amounts of algal attachment were seen for all of the systems.

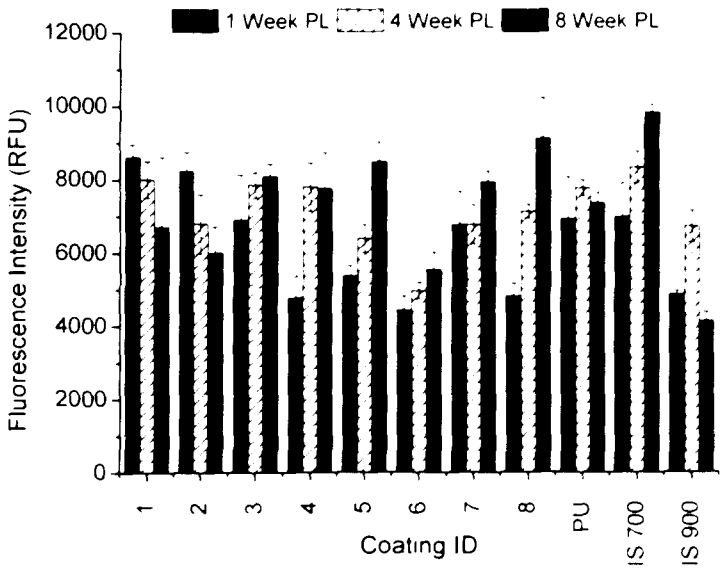


Figure 3.8. Attachment of *N. incerta* to the coating surfaces where the data points are the means of three measurements and the error bars represent one standard deviation of the mean.

The removal of *N. incerta* from the surface of the coatings following water jetting at 10 psi for 10 sec is shown in Figure 3.9. Interestingly, the experimental coatings showed the highest removal of *N. incerta* on the coatings which were

aged for 8 weeks. Coatings 1 and 2 showed removal comparable to the PU control was observed, and this system generally shows a high removal of this diatom. Other coatings, such as coating 3, 4, 7, and 8 showed removal of the organism comparable to the commercial FR coatings while coatings 5 and 6 showed the lowest removal of the diatom.

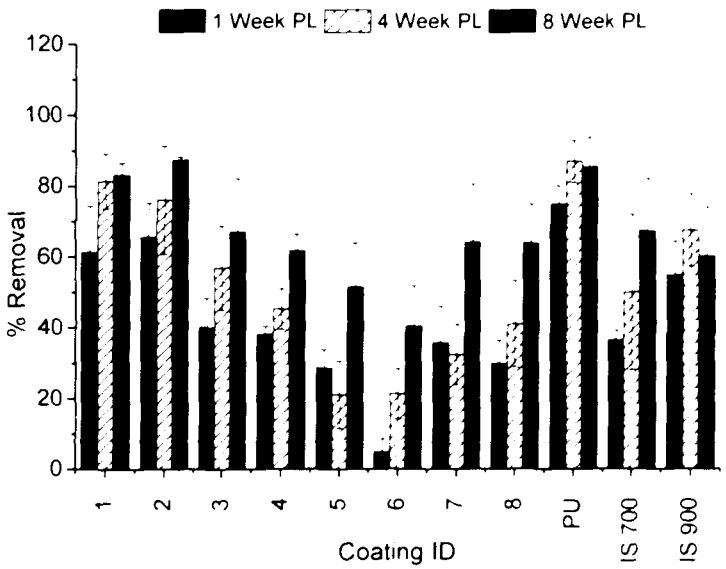


Figure 3.9. Removal of *N. incerta* from the surface of the coatings following water jetting at 10 psi for 10 sec where each data point is the mean of three measurements and the error bars represent one standard deviation of the mean.

Barnacle reattachment data for the coatings is shown in Figure 3.10. The experimental coatings that were aged for 1 and 4 weeks showed low barnacle removal forces that were comparable to those obtained for the IS 700 and IS 900. However, when the coatings were aged for 8 weeks, the barnacle removal forces increased dramatically. The removal forces were comparable to the PU control

coating instead of the commercial FR coatings. This illustrates a change in the coatings or on their surfaces, causing greater barnacle adhesion. Large changes were also found in the SE of the materials when they were measured following extended water aging. Because the water aging was performed in a common tank where degrading coatings were present and biofilm had grown on surface of the coatings prior to analysis, it is difficult to establish whether these differences are due to changes in the coatings or due to other factors.

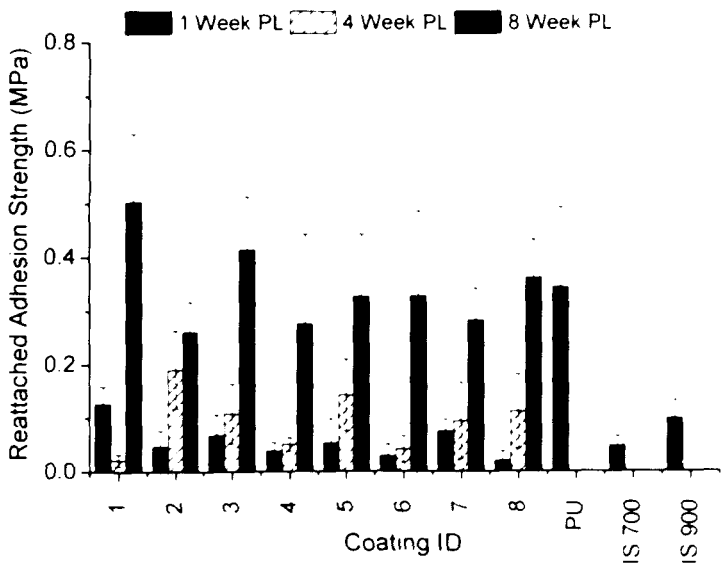


Figure 3.10. Barnacle removal from coating surfaces where the data points each represent a mean of nine measurements and the error bars represent one standard deviation of the mean.

3.4. Summary and conclusions

In this chapter, the properties and fouling-release performance of siloxane-polyurethane coatings that were water aged for periods of 1, 4, and 8 weeks were studied. The results were variable, where some properties were largely affected by

the water aging and others were not. The WCA of the coatings tended to decrease as the coatings were exposed to water aging and the SE of the films also decreased. The PB adhesion was low for all of the coatings exposed to all levels of water aging.

Biological laboratory assays showed variability between compositions and exposure to water aging. *C. lytica* biofilm retention was highest for the coatings prepared with low molecular weight PDMS macromers (coatings 1 and 2), and slightly increased for some compositions exposed to longer water aging cycles. Biofilm retention of *H. pacifica* was moderate in the case of all experimental coatings, and an increase in biofilm retention was observed for some coatings prepared with higher molecular weight of PDMS and exposed to longer water aging. Removal of *H. pacifica* upon water jetting was also reduced for the coatings that were aged in water for 8 weeks. Increased attachment of *N. incerta* was shown for coatings 3, 4, 5, 6, 7, and 8 when they were exposed to water aging for 8 weeks. Removal of *N. incerta* with water jetting was also highest on the coatings that were exposed to 8 weeks of water aging, and two coatings (1 and 2) showed removal similar to that of the PU control. Most other coatings showed performance comparable to IS 700 and IS 900. Removal forces of reattached barnacles were comparable to the commercial FR control coatings when exposed to 1 and 4 weeks of aging. The barnacle adhesion forces increased dramatically upon 8 weeks of aging and were similar to that of the polyurethane control, however.

Most of the results from this study showed changes in properties when the coatings were exposed to extended water aging cycles. This is undesired, as

marine coatings are expected to maintain performance over long periods of time and inconsistency or drop-off in performance and changes in properties could cause major problems for the industry. However, due to bioaccumulation during aging, the results that were observed may not have been due to changes in the coating system, but incomplete removal of other biomass (which may not be encountered in a marine environment) prior to analysis. Aging in the presence of other, possibly less stable coating systems, may have also led to the contamination of the coating surfaces with other organic material. Further analysis of aging of coating systems in an actual marine environment will be discussed further within this dissertation, as samples were prepared for marine field testing. Additionally, the water aging apparatus has been replaced with a more sophisticated system where coatings are aged in individual tanks and the aging water is automatically changed daily.

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CHAPTER 4. FIELD TESTING OF SILOXANE-POLYURETHANE FOULING-RELEASE COATINGS BASED ON PDMS MACROMERS

4.1. Introduction

The natural accumulation of organisms onto surfaces immersed in sea water is problematic for any sea-going vessel. Extensive issues relating to the increased hydrodynamic drag caused by the buildup of organisms on a vessel hull have been identified. These include significant increases in fuel consumption (up to 40%) and resulting emissions, and reduced vessel maneuverability and operating speed, to name a few.[1-3] Antifouling (AF) and fouling-release (FR) paints are the basic methods used to control fouling on a ship hull. AF coatings contain active ingredients which have included biocides such as tributyltin and copper salts.[4] While these coatings are effective in controlling biofouling, environmental concerns have resulted in their decreased popularity. Therefore, FR coatings have gained interest, as they are typically non-toxic and function by minimizing the adhesion of an organism to a surface rather than the inclusion of broad-spectrum biocides often found in AF paints.[5]

Siloxane-polyurethane coatings are a specific type of FR coating composed of polydimethylsiloxane (PDMS) and polyurethane components. The incompatibility of these two materials leads to self-stratification during film formation, resulting in a coating system with a polyurethane bulk and low surface energy PDMS at the surface.[6] The heterogenous morphology of these coating systems is stable in water because it becomes locked into place during crosslinking.[7] Coatings based on this technology have been reported previously to

demonstrate performance comparable to commercial FR standards in laboratory testing.[8] However, to this point, FR data available on these coating systems includes only laboratory testing, and assessment of their performance in a true marine environment is necessary to validate their promise as FR coatings.

More than 4000 marine biofouling organisms have been identified worldwide.[4] The diversity of these organisms, along with the multiple ecological zones they inhabit and globalization of sea-going vessels has increased the difficulty of developing a coating system which is effective in minimizing biofouling. When dealing with FR and AF coatings used to eliminate or reduce fouling, it can be difficult to predict the performance of these materials as hull coatings without testing on vessels in marine environments which requires substantial time and resources.[9] Multiple laboratory assays have been developed and are widely used to screen AF and FR performance rapidly and effectively.[10] These assays, however, are continually challenged in their ability to effectively predict FR performance in the field and only a few publications are available which show their correlation with field testing.[11,12]

In this chapter, the results of several laboratory assays conducted at two universities are compared to multiple assessments of FR performance at three field testing sites. Siloxane-polyurethane coatings were prepared with polydimethylsiloxane (PDMS) macromer (30,000 g/mol) and two polyols which, together with a polyisocyanate, composed the polyurethane bulk. Fouling-release laboratory assays were conducted using a number of known biofouling organisms. The bacteria, *Cellulophaga lytica* (*C. lytica*) and *Halomonas pacifica* (*H. pacifica*)

were used to conduct biofilm retention, retraction and water jet removal bioassays.[12,13] The attachment and removal of the unicellular alga *Navicula incerta* (*N. incerta*) were explored in a similar assay.[14] Sporelings of the green seaweed, *Ulva linza* (*U. linza*) were also used to assess the FR performance of these coatings using water jetting.[15] The lab assays included the adhesion of live reattached adult barnacles to the coating surfaces of which removal with a digital force gauge was used to assess the FR performance of the coatings.[11] Field testing was conducted at three static immersion sites in the United States and Singapore, where the adhesion of slimes and hard fouling were assessed via water jetting, push-off measurements and soft sponging.

4.2. Experimental

4.2.1. Materials

Hexamethylcyclotrisiloxane (D_3), and dimethylchlorosilane (DMCS) were purchased from Gelest Inc. Inhibitor-free tetrahydrofuran (THF), acetylacetone (2,4-pentanedione, PD), lithium trimethylsilanolate (LTMS), allylamine, hydroxylethyl acrylate (HEA), butyl acrylate (BA), methyl amyl ketone (MAK) and chloroplatinic acid hexahydrate were purchased from Sigma-Aldrich. Stabilized THF was received from VWR International. Tolonate® IDT 70B (IDT) was generously provided by Rhodia. Dibutyltin diacetate (DBTDAc) was purchased from Fluka. Capa® 3050 polycaprolactone polyol (PCL) was generously provided by Perstorp. An acrylic polyol (ACR) was prepared in-house (as described below) at 50% solids in toluene. Intergard® 264 primer was received from International Paint and prepared according to manufacturer's specifications.

Standard coating systems were formulated for comparative analysis in the biological fouling-release assays. Intersleek® 700 (IS 700) was prepared according to the manufacturer's specifications. Silastic® T2 (T2) was prepared according to the manufacturer's specifications as well, and was thinned using methyl isobutyl ketone (MIBK) to a pipettable viscosity. A control polycaprolactone polyurethane coating system, formulated without PDMS was also included in the analysis.

The marine bacterium *C. lytica* was generously provided by Dr. Michael Hadfield of the Kewalo Marine Laboratory, University of Hawaii. The marine diatom *N. incerta* was generously provided by the University of Birmingham, UK. Reproductive plants of *U. linza* were collected from Llantwit Major, Glamorgan, Wales, UK (52° 23' N; 3° 30'W). Artificial seawater (ASW) was prepared by dissolving 38.5g of sea salts (Sigma-Aldrich) into 1L of deionized water. Bacterial biofilm growth medium (BGM) consisted of 0.1g yeast extract and 0.5g of peptone per 1L of ASW. Algal growth medium (F/2) consisted of 1L of ASW supplemented with nutrients to generate Guillard's F/2 medium.[16,17] BGM, F/2 and ASW were filter sterilized with 0.2 micron vacuum-cap filters. Crystal violet powder, 33% glacial acetic acid and dimethyl sulfoxide (DMSO) were used as received (VWR International).

4.2.2. PDMS macromer polymerization

A similar synthesis of PDMS macromers has been described previously.[8] A 50% weight solution of D_3 (522 g) was prepared in inhibitor-free THF in a 1000 ml RBF with magnetic stirring at room temperature. The solution was degassed by

bubbling nitrogen gas (N_2) through it for 1 hr. Polymerization initiation was carried out by the addition of LTMS solution (8.5 ml). The polymerization was allowed to proceed at room temperature for 3 hr with magnetic stirring, in a closed N_2 environment. Termination of the polymerization was carried out by the addition of DMCS (2.5 ml). Magnetic stirring was continued overnight to allow for termination of all polymer chains. The resulting hydride terminated PDMS macromer (HT-PDMS-M) was isolated by rotary evaporation and vacuum filtration.

4.2.3. PDMS macromer functionalization

The functionalization of the PDMS macromer via hydrosilylation with allyl amine has been described in Chapter 3. The reaction yields aminopropyl terminated PDMS macromer. Allylamine (3 g) was mixed with a solution of chloroplatinic acid hexahydrate (0.06 g) in inhibitor-free THF (18 g). The solution was heated to 60°C for 1 hr and the mixture was transferred to a 500 ml RBF with HT-PDMS-M (225 g). The reaction mixture was degassed prior to heating to 90°C for 24 hr. The completion of reaction was determined by the absence of the silicon hydride peak at 4.7 ppm in proton nuclear magnetic resonance spectroscopy (^{1}H-NMR). Following functionalization, the brown reaction mixture was rotary evaporated to remove excess allylamine and residual THF. The brown color was lessened by extraction with methanol and stirring in the presence of activated carbon.

4.2.4. Acrylic polyol polymerization

The preparation of a hydroxyl functional acrylic polymer was carried out using a starved-feed free radical polymerization in toluene. The reaction apparatus

consisted of a 5000 ml four-neck round bottom flask fitted with a condenser, overhead mechanical stirrer, nitrogen inlet and thermocouple, and a monomer pumping inlet. Toluene (960 g) was initially charged with toluene and heated to 80°C. A previously prepared and refrigerated monomer mixture of butyl acrylate (1200 g) and hydroxyethyl acrylate (300 g) was mixed with a previously prepared and refrigerated free radical initiator solution of Vazo® 67 (60 g) in toluene (540 g) immediately prior to use. The addition of the monomer and initiator mixture was carried out over approximately 3 hr at a feed rate of 12-13 ml min^{-1}, with the reaction temperature maintained in the range of 90-100°C. Following monomer/initiator addition, the reaction temperature was maintained for 30 min and then a chaser solution of Vazo® 67 (6 g) in toluene (54 g) was added. The reaction temperature was maintained for one hour, and then cooled to room temperature with mechanical stirring. The final polymer was 50% solids in toluene.

4.2.5. Characterization of PDMS macromers and acrylic polyol

4.2.5.1. Symyx® Rapid GPC: High-throughput gel permeation chromatography (GPC) was used to determine the approximate molecular weight of polymers used in this study, relative to polystyrene standards. Analysis was performed using polymer solutions at 2 mg ml^{-1} in stabilized THF, a Symyx® Rapid GPC, an evaporative light scattering detector (PL-ELS 1000), 2xPLgel mixed-B columns (10 μm particle size) and a 2.0 ml min^{-1} flow rate.

4.2.6. Siloxane-polyurethane coating formulation

The siloxane-polyurethane coating formulations were prepared by first pre-mixing the APT-PDMS-M and the IDT overnight to ensure that all PDMS chains

would be reacted into the coating. The following day, the DBTDAc solution, polyol solution, and PD were added, with stirring between additions. The amounts of each component used in the formulation of the siloxane-polyurethane coatings are also outlined in Table 4.1. All formulations were mixed by magnetic stirring for 1 hr prior to coating application.

Table 4.1. Components and amounts used in the formulation of siloxane-polyurethane coatings.

	APT-PDMS-M	Tolonate IDT 70B	Polyol			DBTDAc Solution	PD
Coating	(g)	(g)	Type	Solution	(g)	(g)	(g)
PCL-M10	13.0	113.2	PCL	90% in MAK	42.0	1.3	16.9
PCL-M20	26.0	100.7	PCL	90% in MAK	37.3	1.3	16.5
ACR-M10	10.0	50.6	ACR	50% in Toluene	109.1	1.0	17.1
ACR-M20	20.0	45.1	ACR	50% in Toluene	96.8	1.0	16.3

4.2.7. Siloxane-polyurethane coating preparation and curing

The coatings were prepared in 24-well plates on aluminum disks and on aluminum Q-panels (4 x 8 in., 0.6 mm thick, type A, alloy 3003 H14, obtained from Q-lab) which had been bead blasted and primed with Intergard 264 (70-80 μm primer thickness) via air-assisted spray application. In 24-well plates, 250 μl was deposited into each well and gentle agitation ensured the coverage of the entire primed aluminum disk. On panels, the coatings were applied using an 8 mil gap drawdown bar, with a 3 in. coating path. The entire length of the panels were coated, while the vertical edges of the panels were not coated (due to the 3 in.

drawdown bar width), and some exposed primer was present along those edges and at the top of the panels. The coatings were ambient cured overnight and oven cured the following morning at 80°C for 45 min.

4.2.8. Characterization of siloxane-polyurethane coating physical properties

4.2.8.1. Contact angle and surface energy (SE) analysis: SE analysis was performed on a Symyx® Coatings Surface Energy System with First Ten Ångstroms™ software. Three contact angles of each water and methylene iodide were measured on the surfaces of the coatings. Photographs of each droplet were taken with a CCD camera and automated image analysis was used to measure the wetting angle. The mean contact angles of each liquid were used to calculate the surface energy of each coating using the Owens-Wendt method.[18]

4.2.8.2. Pseudobarnacle (PB) adhesion: The removal forces required to remove epoxy-glued studs (pseudobarnacles) from the surface of the coatings were measured using a Symyx® Automated Pull-Off Adhesion station.[19] In preparation for the test, the panels were held in place by a vacuum plate and covered with a plastic template with 24 patches of three 7 mm holes. Two-component epoxy adhesive (Loctite® Hysol® 1C-LV) was deposited onto the coated panels, by spreading it over the plastic template using a putty knife. The panels were placed into clamping jigs, PBs were applied, and foam blocks were placed atop the PBs for curing of the adhesive. Following overnight curing of the adhesive, the clamping jigs were placed in the automated adhesion station where an automated head removed the PBs by applying gradual force.

4.2.9. Assessment of siloxane-polyurethane fouling-release performance via laboratory assays

4.2.9.1. Coating Pre-leaching: The coatings were pre-leached by water immersion to allow for any toxic leachates which could have been present in the coatings to be removed. The coatings were pre-leached in a clean, recirculating water tank where the water was automatically changed daily. After pre-leaching, the coatings were allowed to dry under ambient conditions. The coatings used in the bacterial, microalgae diatom and barnacle bioassays were pre-leached for four and eight weeks (one set of coatings for each pre-leach time) and the coatings used in the sporelings bioassay were pre-leached for 14 days prior to analysis.

Leachate toxicity

Leachate toxicity analysis was performed on the coatings following pre-leaching to ensure that all potentially toxic materials had been removed from the coatings prior to analysis.[20] Coating extractions were performed in 24-well plates where the coatings had been deposited. Bacterial and microalgae diatom growth was monitored in the presence of ASW and nutrients for 24 hr. The bacterial growth was monitored by staining with crystal violet and quantified by extraction of the stain and absorbance measurements at 600 nm. Microalgae diatom growth was quantified by fluorescence measurements (excitation wavelength: 360 nm, emission wavelength: 670 nm). The bacterial and diatom growth in the presence of the experimental coatings was compared to negative growth controls and results of leachate toxicity analysis of standard coatings to confirm that the coatings did not contain toxic leachates which could interfere with biological analysis.

For leachate toxicity using *Ulva* sporelings, the coatings were pre-leached for an additional 48 hr in distilled water. One milliliter of ASW was added to one row of each coating (6 replicates) and plates were gently shaken (60 movements/min) for 18 hr. The ASW was removed and transferred to untreated 24-well plates. To each well, 1 ml *Ulva* spore suspension (5 x 10^5 spores ml^{-1}) in double strength enriched seawater medium was added. The plates were incubated for 2 hr in darkness at room temperature before being transferred to an illuminated incubator at 18°C with a 16:8 light: dark cycle (photon flux density 45 µmol m^{-2} s^{-1}). After 7 days of growth, the seawater medium was removed from the wells and the chlorophyll was extracted from the attached biomass. The mean percentage inhibition (6 replicates) compared to a seawater control was calculated. Chlorophyll extraction and fluorescence measurements were performed as described for *Navicula*. The coatings were determined to be non-toxic prior to analysis.

4.2.9.2. Bacterial biofilm retention, retraction and removal: High throughput analysis of *C. lytica* and *H. pacifica* biofilm retention was performed using coatings deposited in 24-well plates where three replicates were tested per coating system. This bioassay has been previously described.[21] The wells were inoculated with 1.0 ml of a bacterial suspension (*C. lytica*: 10^7 cells ml^{-1} in BGM, *H. pacifica*: 10^8 cells ml^{-1} in ASW) and the plates were incubated for 24 hr at 28°C. Following incubation, the BGM and planktonic growth were discarded and the wells were rinsed with ASW three times to remove unattached or weakly adhered biofilm. The plates with retained bacterial biofilm were dried for 1 hr under ambient conditions. The biofilm was stained with crystal violet (0.3% w/v in deionized water) and

surface coverage was measured using analysis of grayscale images with PhotoGrid 1.0 software (University of Hawaii) to determine biofilm retraction. Biofilm retraction was not observed for *H. pacifica*, and therefore was not measured. Extraction of crystal violet with 0.5 ml of 33% glacial acetic acid and quantification by absorbance measurements at 600 nm were used to determine biofilm retention where the absorbance values were considered to be directly proportional to the amount of biofilm retained on the coating surfaces.

Removal of bacteria was carried out by exposing retained biofilms to water jetting using an automated, rotating water jet.[13] For each coating, three wells were inoculated and incubated as described above. Growth media and planktonic growth were discarded and the coatings were rinsed three times with ASW to remove unattached, or weakly adhered cells. Four replicate wells inoculated with *C. lytica* were water jetted at 20 psi for 5 sec and three replicate wells inoculated with *H. pacifica* were subjected to water jetting at 20 psi for 5 sec. The biofilm unremoved by the water jet was quantified by staining, extraction, and quantification with crystal violet. Biofilm retention on untreated coatings served as initial cell attachment to the coatings for the calculation of biofilm removal by water jet.

4.2.9.3. N. incerta *attachment and removal:* The microalgae diatom removal assay was carried out in high throughput and has been described previously.[14] Coatings deposited in 24-well plates were inoculated with 1.0 ml of *N. incerta* suspension (10^5 cells ml^{-1}) in F/2 and incubated for 2 hr at room temperature. Removal of the microalgae diatom was carried out by water jetting. Four replicates

of each coating were water jetted at 20 psi for 10 sec using an automated, rotating water jet. Four replicates wells of each coating were left untreated and served as initial attachment measurements. To each well, 0.5 ml of DMSO was added and the plates were incubated in darkness for 30 min to extract chlorophyll. Gentle agitation of the plates was carried out to obtain a homogeneous solution. The solution was transferred (0.2 ml) to a 96-well plate for fluorescence measurements using a spectrophotometer designed for reading multi-well plates (excitation wavelength: 360 nm, emission wavelength: 670 nm). The removal of the diatom was recorded as the difference in relative fluorescence units (RFU) between the untreated wells and those treated with the water jet.

4.2.9.4. Ulva *sporeling removal:* The *Ulva* sporeling removal assay has been previously described.[22] Coatings were equilibrated in deionized water for 48 hr and subsequently in ASW for 2 hr prior to analysis. *Ulva* spores were release into ASW (pH 8.0, 32%) and the concentration of the sporelings suspension was adjusted to 5×10^5 spores ml^{-1}. For this assay, 24-well plates were used in which the same coating was deposited into all wells. Each well was inoculated with 1 ml of the spore suspension and the plates were incubated in the dark for 2 hr. Following incubation, the plates were washed to remove unattached spores. The retained spores were grown for 7 days in an illuminated incubator at 18°C with a 16:8 light: dark cycle (photon flux density: 45 µmol m^{-2} s^{-1}) and the nutrients were renewed every 48 hr. Following the growth period, six replicate wells were exposed to each 18, 67, and 111 kPa water jetting. Six replicate wells were left untreated and served as the initial attachment of spores. The spores present with

and without water jetting were determined by extraction and quantification of chlorophyll, as described for *Navicula*. Removal of the spores was calculated as the difference between initial attachment and remaining spores after water jetting.

4.2.9.5. Barnacle reattachment: The FR performance of the coatings was examined for shell fouling with a live adult barnacle (*Amphibalanus amphitrite* = (*Balanus amphitrite*)) reattachment assay, as previously described.[11] Nine adult barnacles approximately 5 mm in diameter were transferred from a silicone elastomer (Silastic-T2 on glass) to the surface of each coating. The barnacles were placed in an aquarium system with ASW for 14 days and were fed nauplii shrimp daily. The adhesive forces of the reattached barnacles were measured using a hand held digital force gauge in accordance with ASTM D5618-94. The force gauge was placed at the base of the barnacles (parallel to coating surface) and gradual lateral pressure was applied until the barnacle became dislodged from the coating surface. The barnacle base plate areas were measured using image analysis (Sigma Scan Pro 5.0). The barnacle adhesive strengths were calculated from the removal forces and areas of the barnacle base plates. Reported adhesion forces included barnacles for which measurable forces were obtained, and broken barnacles were not included in any reported values.

4.2.10. Assessment of siloxane-polyurethane coating fouling-release performance via marine field testing

4.2.10.1. Immersion at Californic Polytechnic University (Cal Poly): Four replicates of each coating system were immersed at the Cal Poly test site, located near the mouth of Morro Bay in a temperate marine environment. The site consists

of a floating dock that is raised and lowered with the tidal cycle so the panels remain at a constant depth of 2-3 feet. Typical temperature and salinity fluctuations are seasonal and range from 11.2-22.3°C and 13-35%, respectively. Morro Bay's fouling community is diverse and changes seasonally. Barnacle recruitment usually occurs from summer to early fall and late winter to spring. The heaviest fouling occurs between spring and fall. The fouling community consists of sponges, tunicates, tubeworms, hydroids, anenomes, tube-dwelling amphipods, arborescent and encrusting bryozoans and several species of barnacles, the most abundant of which is *Balanus crenatus.* The most dominant species is an invasive enrcrusting bryozoan *Watersipora subtorquata.*

4.2.10.2. Water jetting of coatings at Cal Poly: Adhesion of fouling organisms was measured using a water jet. The test apparatus consisted of a modified SCUBA tank that was filled with seawater connected to another SCUBA tank filled with compressed air via a regulator hose, which allowed the pressure of the water leaving the tank to be controlled. A hose was connected to the pressurized water tank and had another regulator at the nozzle which allowed water pressure to be controlled at the working end. The pressurized stream of water was applied to the surface of the panel through the nozzle at a series of water pressures (40, 80, 120, 180 and 240 psi). The water stream was applied perpendicular to and approximately one inch away from the surface as evenly as possible across the entire surface of the panel. One replicate of each panel type was tested monthly using the water jet. Prior to testing, percent coverage of each fouling category (slime, soft or hard) was estimated and organisms present were

recorded. Each panel was sprayed at each of the water pressures listed above and percent coverage of each fouling category was visually estimated after each pressure is applied. After the maximum pressure was applied, remaining organisms were noted. Digital photos were taken before and after water jet testing.

4.2.10.3. Barnacle adhesion at Cal Poly: The method used for measuring barnacle adhesion is based on ASTM D 5618-94. Shear force was applied to the base of the barnacle using a hand held force gauge, at the approximate rate of 4.5 N sec^{-1}. The force at which the barnacle detached from the surface was recorded. Basal diameters were measured in the field using calipers and are used to calculate the basal plate area. The critical removal stress (CRS) was calculated by dividing the force of removal by the surface area of the basal plate. Barnacles that broke upon removal and left behind greater than 10% of their basal plate were not included in calculating CRS but are recorded and used to help evaluate panel efficacy by calculating percentage of broken barnacles of those on which removal was attempted.

4.2.10.4. Immersion at Florida Institute of Technology (FIT): Four replicates of each coating system were exposed at the Florida Institute of Technology static immersion site in the Indian River Lagoon on May 30, 2009. Digital photographs were taken. All panels were held 1 meter below the surface and caged to prevent predation. The eleven treatments were randomized on two frames and panels were placed back to back.

4.2.10.5. Water jetting of coatings at FIT: A water jet apparatus which has been previously described was used where a SCUBA air tank was assembled in

parallel with a SCUBA tank containing sea water and a pressure regulator allowed for setting the water jet pressure for field testing analysis.[23] The initial water jet pressure was set to 50 psi. A patch (approximately 1 in. by 1.5 in.) was selected based on biofilm presence and macrofouling absence and sprayed until it was determined that no more biofilm was being removed. If the patch was not cleaned, the pressure is raised by 30 psi and spraying was repeated. This was continued until the patch was clean or until the maximum pressure (200 psi) was achieved. The removal is determined visually.

4.2.10.6. Barnacle adhesion at FIT: A shear force was applied to the base of adult barnacles using a digital force gauge, following ASTM D5618-94. The force required for removal of each barnacle was recorded and the base area of the organism was determined using a digital scanner. The shear strength was determined by dividing the removal force by the base area of the barnacle base plate.

4.2.10.7. Immersion at National University of Singapore (NUS): Four replicates of each coating system were immersed at the NUS test site. All panels were randomized and arranged in a 2-tier block fashion, at a depth of 0.50 m for the upper tier and 0.70 m for the lower tier. The distance between adjacent coatings was kept at 40 mm. The test was carried out in a caged well to reduce fish grazing.

4.2.10.8. Soft sponging at NUS: Panel assessment was performed once per month. Digital photos of the fouled panels were taken before and after soft sponging to assess the FR performance of the coatings.

4.3. Results and discussion

Four siloxane-polyurethane coatings were prepared for assessment of FR performance by laboratory assays and field testing. Table 4.2 summarizes the composition of the cured coatings, where the polyol type and PDMS content were varied and the molecular weight of the APT-PDMS-M was the same for all coatings. The coatings were deposited into 24-well plates for lab assays at North Dakota State University (NDSU) and University of Birmingham. The coatings were also prepared as drawdowns onto 4 x 8 in. primed aluminum panels for static immersion at field testing sites at California Polytechnic University (CalPoly), Florida Institute of Technology (FIT), and National University of Singapore (NUS). The coatings were compared to commercial FR standards (IS 700 and IS 900), a silicone standard (T2), and a polyurethane control prepared without PDMS.

Table 4.2. Solid mass percent composition of cured siloxane-polyurethane coatings where the loading of PDMS and polyol type were varied.

Coating ID	APT-PDMS-M Mass %	Polyol Type	Mass %	IDT Mass %
PCL-M10	10.0%	Polycaprolactone	29.1%	60.9%
PCL-M20	20.0%	Polycaprolactone	25.8%	54.2%
ACR-M10	10.0%	Acrylic	54.6%	35.4%
ACR-M20	20.0%	Acrylic	48.4%	31.6%

4.3.1. Polymer and siloxane-polyurethane coating properties

The molecular weight distributions, as determined by gel permeation chromatography (GPC), for the PDMS polymers used in the preparation of the siloxane-polyurethane coatings are shown in Table 4.3. As indicated, the molecular weights of APT-PDMS-M was in the range of the target molecular

weight (relative to polystyrene standards). The molecular weight distribution was within the expected ranges, as it was prepared via living anionic polymerization.

Table 4.3. GPC data for the PDMS polymers used in the preparation of siloxane-polyurethane FR coatings.

Polymer	Target MW (g/mol)	$\overline{M_n}$	$\overline{M_w}$	PDI
APT-PDMS-M	30,000	28,400	31,800	1.1

The water contact angles (WCA) and surface energies (SE) of the cured coatings are shown in Figure 4.1. The siloxane-polyurethane coatings showed high WCA, where the mean WCA were in the range of 105-111° for all of the coatings. The SE of the cured coatings were also low (14-23 mN/m), as expected for these types of systems where PDMS has migrated to the coating surface. The polyol did not affect the WCA or SE of the coatings. The WCA of the polycaprolactone polyurethane (PCL-PU) control (82°) was considerably lower than the coatings prepared with either type of PDMS. The SE of the PCL-PU control (41 mN m^{-1}) was also much higher than for the siloxane-polyurethane coatings. This was expected, as the self-stratification of these coatings results in a PDMS-rich surface, higher WCA and lower SE compared to the PU control. The pseudobarnacle (PB) adhesion for these coatings and commercial fouling-release controls is shown in Figure 4.2. The PB adhesion force for the siloxane-polyurethane coatings were similar for all of the systems (7-10 N). The siloxane-polyurethane coatings showed PB removal forces in the range of the commercial standards (9 N), and greatly reduced from the PCL-PU (90 N).

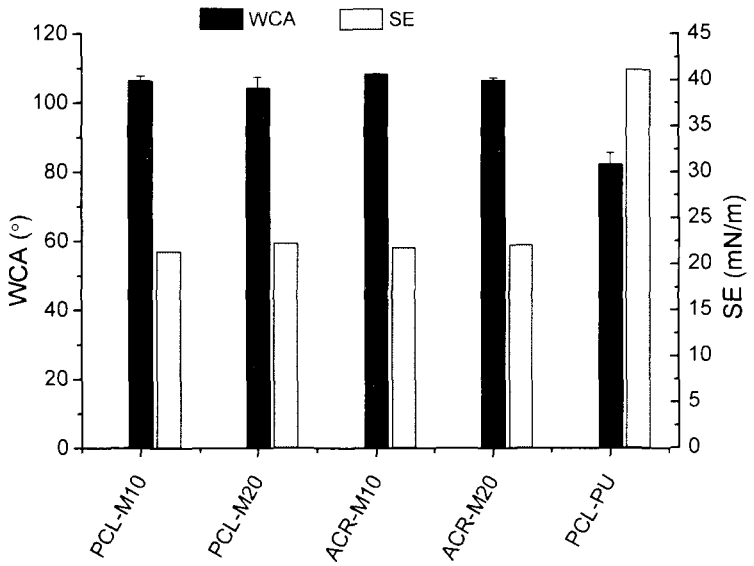

Figure 4.1. WCA and SE of siloxane-polyurethane coatings. The WCA data is the mean of three measurements and the error bars represent one standard deviation of the mean. SE was calculated using the mean values of three WCA and three methylene iodide contact angle (MICA) measurements using the Owens-Wendt method.[18]

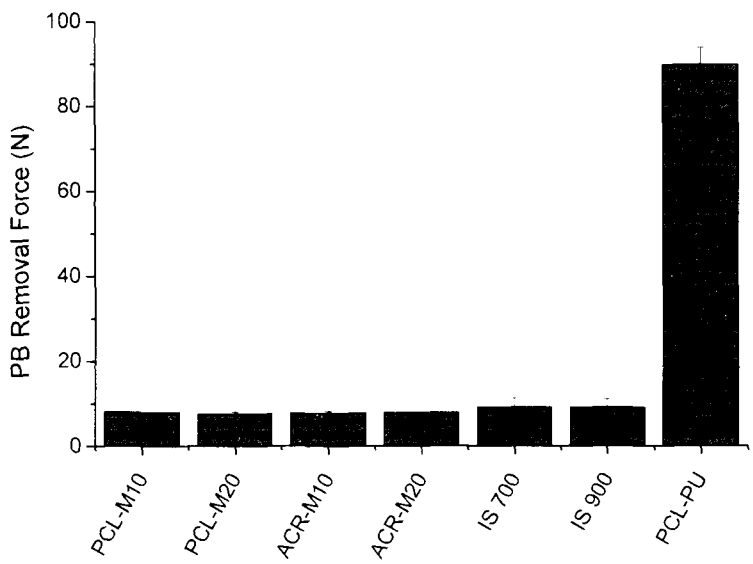

Figure 4.2. PB adhesion of siloxane-polyurethane coatings where the values are the means of at least three measurements and the error bars represent one standard deviation of the mean.

4.3.2. Assessment of siloxane-polyurethane fouling-release performance via laboratory assays

The FR performance of the siloxane-polyurethane coatings was analyzed using various laboratory assays to assess the biofilm retraction and removal of the marine bacteria *C. lytica* and biofilm removal of the marine bacteria *H. pacifica*, the microalgae diatom *N. incerta*, the algal sporelings of *U. linza*, and adult barnacles of *A. amphitrite*. With the exception of the *U. linza* assay, the analysis was performed at North Dakota State University on coatings which were pre-leached (PL) in water for four or eight weeks. The coatings used in the *U. linza* assay were water aged for two weeks prior to analysis performed at University of Birmingham (UK). In all cases, the coatings were found to be non-toxic in leachate toxicity analysis prior to evaluating their FR performance. The barnacle reattachment assay was conducted on coated panels while the other tests were performed in 24-well plates. The results from these assays are outlined in the sections to follow.

4.3.2.1. Biofilm retraction, retention and removal of C. lytica *bacteria:* Biofilm retention of *C. lytica* on siloxane-polyurethane coatings is shown in Figure 4.3 and biofilm retraction of *C. lytica* on the coating surfaces is shown in Figure 4.4 as percent surface coverage. The coatings prepared with ACR polyol showed higher retention of *C. lytica* on the coating surface and the same coatings showed a reduction in surface coverage by the bacteria. This suggests low affinity for these coatings, as it stacked upon other bacteria instead of spreading over the surface. Similar biofilm retention was observed compared to the FR controls, where PCL-M10 and PCL-M20 showed similar retention as IS 900 and ACR-M10 and ACR-

M20 showed similar retention as IS 700. Pre-leaching time did not affect the biofilm retention on the coatings, but a reduction in biofilm retraction was observed for PCL-M10 and PCL-M20 after 8 week PL, compared to 4 week PL.

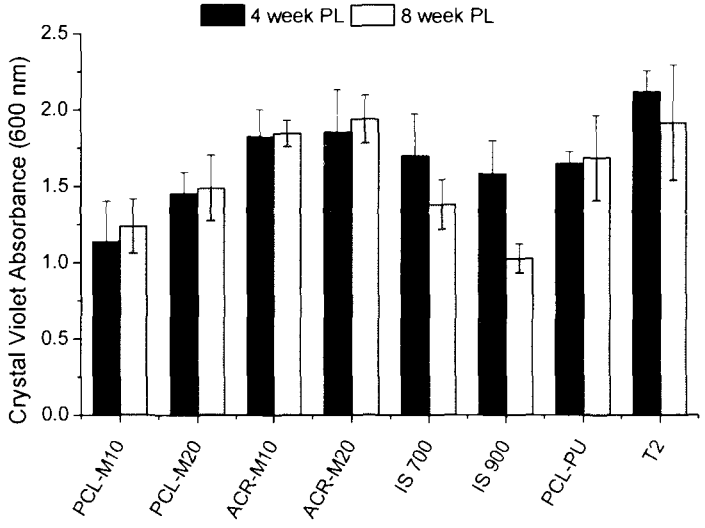

Figure 4.3. Biofilm retention of *C. lytica* where the values shown are the means of three measurements and the error bars represent one standard deviation of the mean.

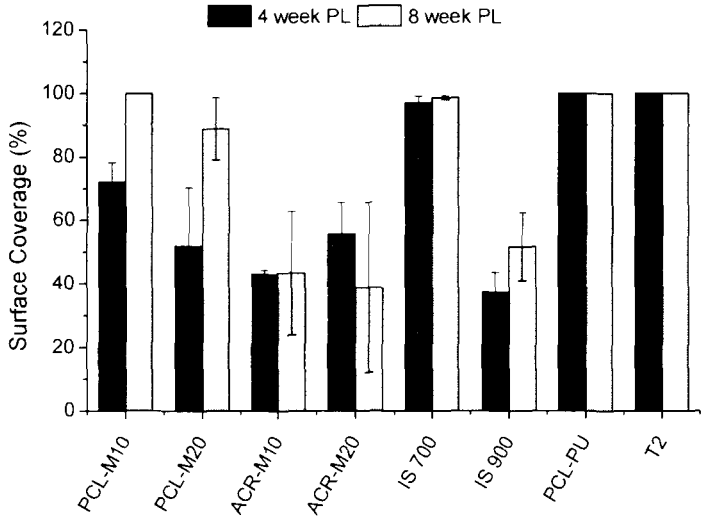

Figure 4.4. Biofilm retraction of *C. lytica* where the values shown are the means of three measurements and the error bars represent one standard deviation of the mean.

The removal of *C. lytica* biofilm from the coating surfaces with water jetting at 20 psi for 5 sec is shown in Figure 4.5. IS 900 showed the highest bacterial removal near 100% at both 4 and 8 week PL. IS 700 showed 70-80% removal of the bacteria at 4 and 8 weeks of PL, and this was comparable to the bacterial removal observed for the siloxane-polyurethane coatings. PCL-M20 showed complete removal of the bacteria after 4 week PL, and this performance was similar to IS 900.

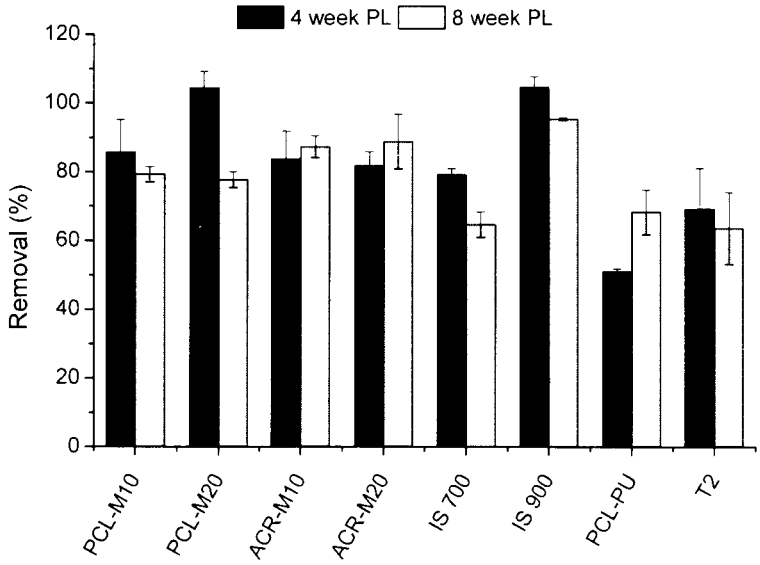

Figure 4.5. Removal of *C. lytica* from siloxane-polyurethane coatings upon water jetting at 20 psi for 5 sec. The values shown are the means of three measurements and the error bars represent one standard deviation of the mean.

4.3.2.2. Attachment and removal of N. incerta *diatoms:* Attachment of *N. incerta* on the coating surfaces is shown in Figure 4.6. Removal of *N. incerta* from the coating surfaces with water jetting at 20 psi for 10 sec is shown in Figure 4.7. Attachment of the diatoms onto these coatings was similar for most of the

coatings, and to that observed for the FR controls. For some coatings, slightly higher attachment was observed on coatings that were PL for 8 weeks compared to 4 weeks. Removal of the *N. incerta* slime (55-62%) from the siloxane-polyurethane coatings was comparable to IS 700 and IS 900 at 4 and 8 weeks PL, and the PL time did not affect the removal of the organism. The PCL-PU control showed the highest level of diatom removal, which is common in these types experiments, as this organism is known to adhere well to silicone FR coatings.

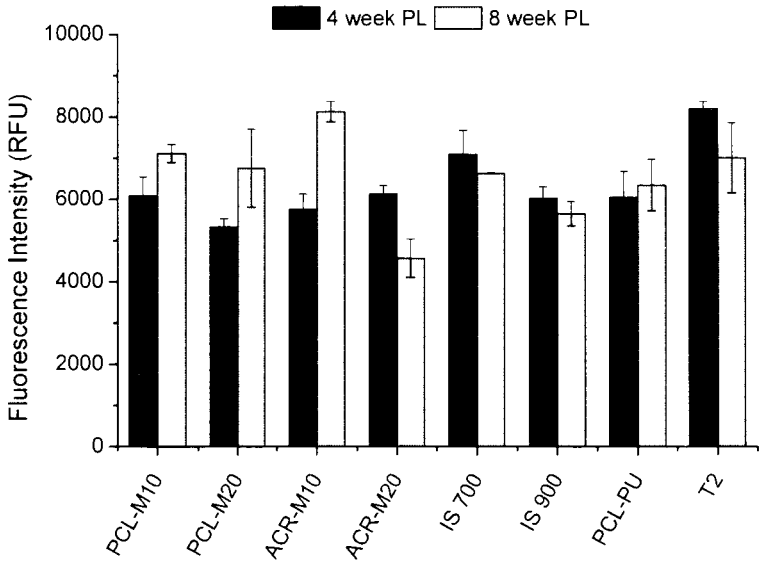

Figure 4.6. Attachment of *N. incerta* on siloxane-polyurethane coatings where the values shown are the means of three measurements and the error bars represent one standard deviation of the mean.

4.3.2.3. Biofilm retention and retraction of H. pacifica *bacteria:* Biofilm retention of *H. pacifica* on the siloxane-polyurethane and standard coatings is shown in Figure 4.8. Removal of *H. pacifica* from the coating surfaces is shown in Figure 4.9 after water jetting at 25 psi for 5 sec. The siloxane-polyurethane

coatings showed slightly higher biofilm retention of *H. pacifica* compared to the FR standards. However, the removal of the bacteria was greater from the siloxane-polyurethane coatings compared to the FR standards in most cases, even though low removal was observed. The coatings prepared with the PCL polyol showed greater release of *H. pacifica* compared to those prepared with the ACR polyol while the PCL-PU showed the highest removal of *H. pacifica* after 4 (74%) and 8 (85%) weeks of PL.

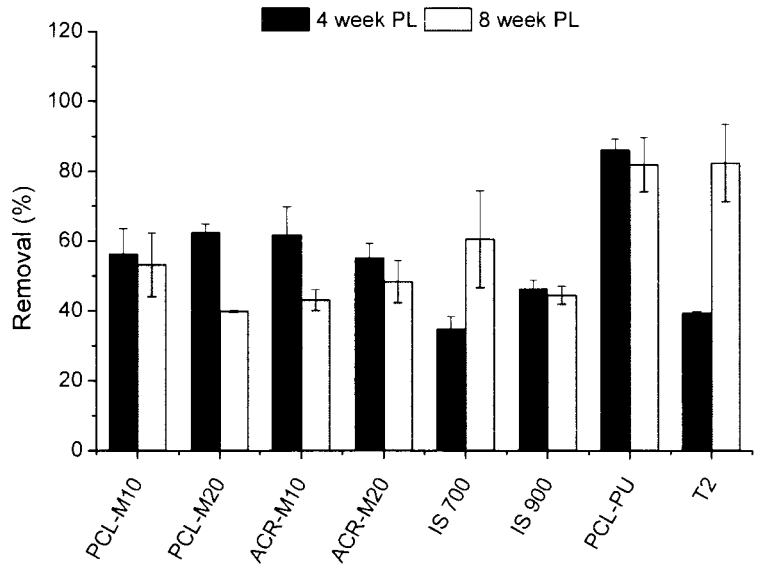

Figure 4.7. Removal of *N. incerta* upon water jetting at 20 psi for 10 sec. The values shown are means of three measurements and the error bars represent one standard deviation of the mean.

4.3.2.4. Attachment and removal of U. linza *zoospores:* The attachment to and removal of *U. linza* from the coatings upon water jetting are shown in Figures 4.10 and 4.11, respectively. Attachment on the siloxane-polyurethane coatings was similar to the attachment observed for the FR standards. The siloxane-

polyurethane coatings showed sporeling removal comparable to IS 900 and greater than IS 700 at all water jetting pressures. While PCL-M20 showed the highest sporeling removal at 18 kPa, the lowest water jetting pressure, the siloxane-polyurethane showed similar overall performance that was comparable to IS 900.

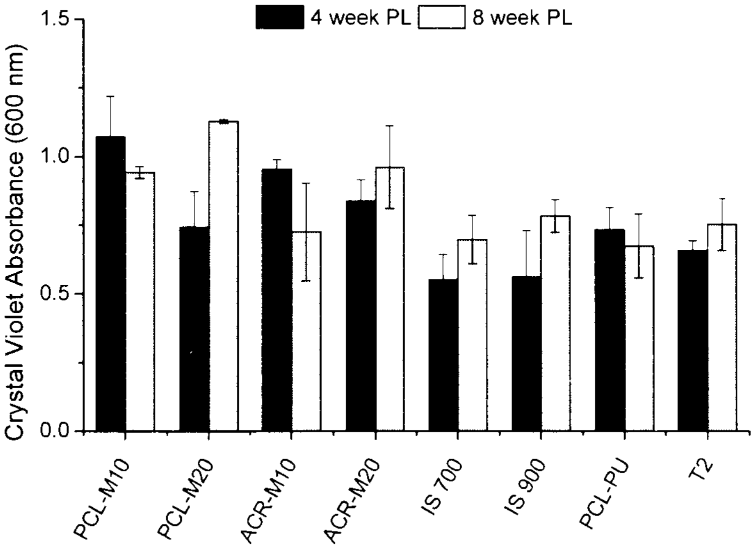

Figure 4.8. Biofilm retention of *H. pacifica* where the values shown are the means of three measurements and the error bars represent one standard deviation of the mean.

ent: The reattached adhesion of adult barnacles jure 4.12 where the removal of nine barnacles l of the siloxane-polyurethane coatings showed on than the commercial FR coatings and silicone e of barnacles from the PU-PCL appears to be ne coatings, only one barnacle was able to be

measured on the PCL-PU coating, due to shell breakage during testing. The siloxane-polyurethane coatings showed release of most barnacles tested, even though the removal force was elevated compared to controls. Coating PCL-M20 showed the lowest mean removal force of the other siloxane-polyurethane coatings, and the highest number of measurable barnacles. PCL-M10 also showed low barnacle removal force, but few barnacles were removed without breaking at 4 week PL. In most cases, the PL time did not seem to affect the barnacle adhesion or the number of measurable barnacles. There was not a large difference in barnacle adhesion with respect to the type of polyol used in the coating.

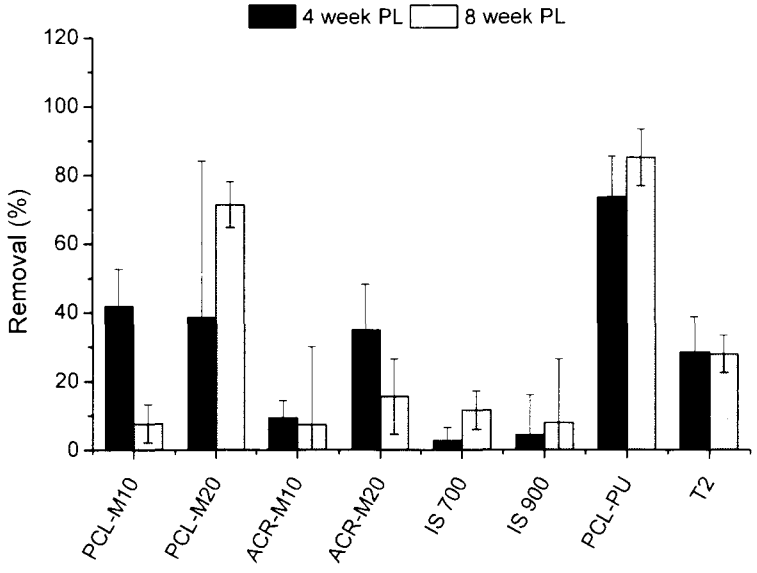

Figure 4.9. Removal of *H. pacifica* from siloxane-polyurethane coatings upon water jetting at 25 psi for 5 sec. The values shown are the means of three measurements and the error bars represent one standard deviation of the mean.

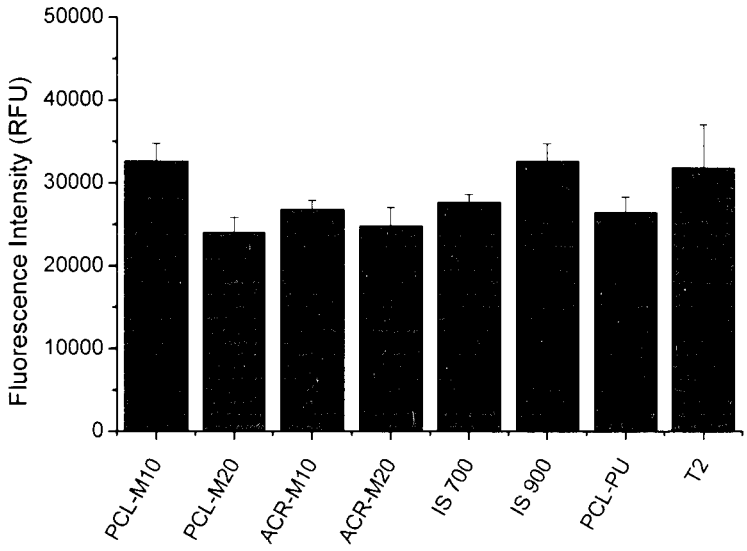

Figure 4.10. Attachment of *U. linza* zoospores where the values shown are the means of six measurements and the error bars represent 95% confidence intervals derived from arcsine transformed data.

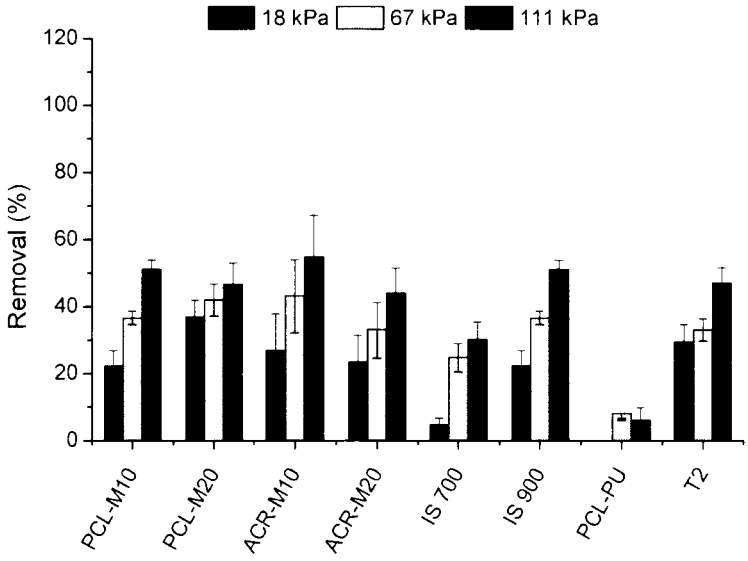

Figure 4.11. Removal of *U. linza* zoospores upon water jetting. The values shown are the means of six measurements and the error bars represent 95% confidence intervals derived from arcsine transformed data.

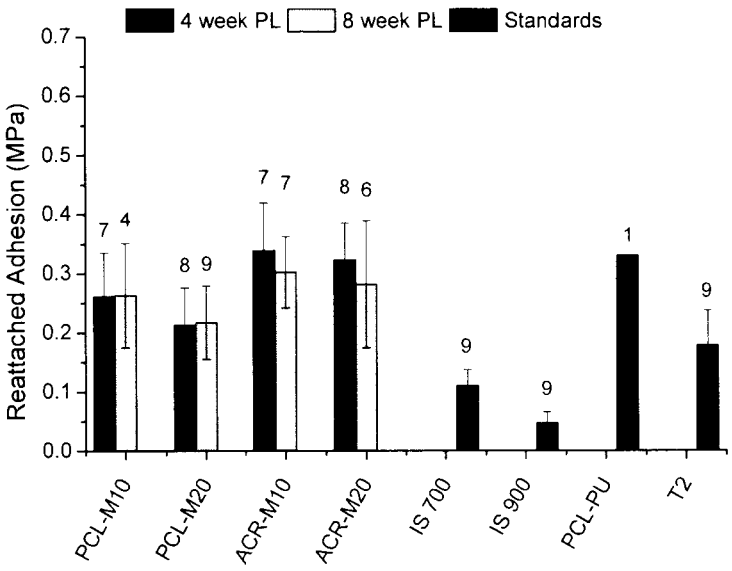

Figure 4.12. Barnacle reattachment adhesion where the values shown are the means of the number of barnacles shown when nine measurements were attempted. The error bars represent one standard deviation of the mean.

4.3.3. Assessment of siloxane-polyurethane fouling-release performance via marine field testing

The FR performance of the siloxane-polyurethane coatings was also analyzed at three field testing sites. At CalPoly, water jetting of slime and hard fouling was performed at 1, 3, and 6 months, and barnacle adhesion was measured periodically as appropriately sized barnacles were observed. At FIT, water jetting was performed on initial slime fouling (24 days of immersion), and barnacle adhesion was performed after 76 days of immersion.

The removal of slimes and hard fouling via water jetting after one month of immersion at the Morro Bay site at CalPoly is shown in Figure 4.13 where the water jet pressure for the complete removal of the fouling is shown. The soft

fouling on the siloxane-polyurethane coatings was removed at the same water jet pressure as for IS 700 and IS 900 and soft fouling PCL-M10 was removed at a lower pressure than the FR standards. Hard fouling on PCL-M20 was removed at the same water jet pressure as for IS 700 and IS 900, while the other coatings (PCL-M10, ACR-M10 and ACR-M20) required a higher water jet pressure. While hard fouling showed stronger adhesion on the siloxane-polyurethane coating, the ease of removal for soft fouling shows promising FR performance.

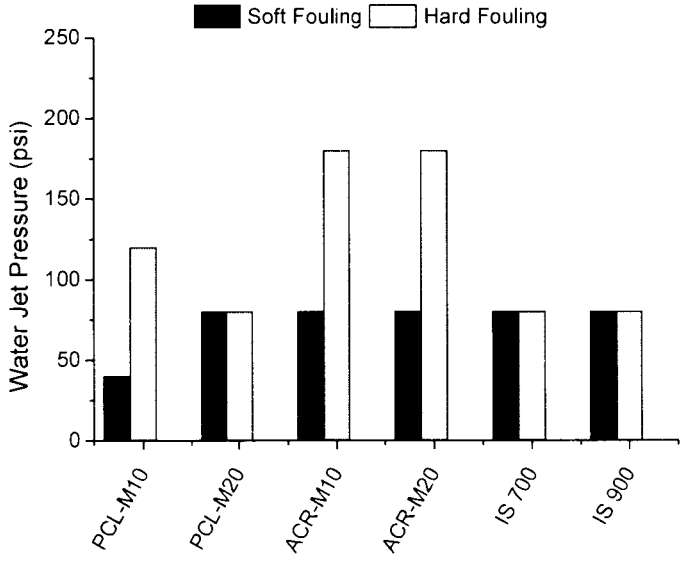

Figure 4.13. CalPoly water jetting on a single replicate panel after one month of immersion where the water jet pressure required for the removal of 100% of the fouling is shown.

The removal of slime on panels immersed at Cal Poly's field testing site after three and six months of immersion is shown in Figure 4.14 where the remaining slime after water jetting at 240 psi is reported. Higher levels of remaining indicate that the FR performance was not as good as was observed after one

month of immersion, where 100% of fouling was removed at lower water jet pressures. At three months of immersion, the siloxane-polyurethane coatings showed a greater amount of slime remaining after water jetting compared to IS 700 and IS 900. After six months of immersion, the siloxane-polyurethane coatings had less slime remaining after water jetting, and the slime that remained was less than at three months of immersion. Following water jetting at 6 months of immersion, there was less slime remaining on the siloxane-polyurethane coatings compared to IS 700 and IS 900. While IS 700 and IS 900 showed better FR performance at three months of immersion, the siloxane-polyurethane coatings showed better performance after six months of immersion. The siloxane-polyurethane coatings showed promising FR performance for the removal of slime at up to six months of immersion and the coatings prepared with 20% PDMS showed slightly improved performance over those prepared with 10% PDMS.

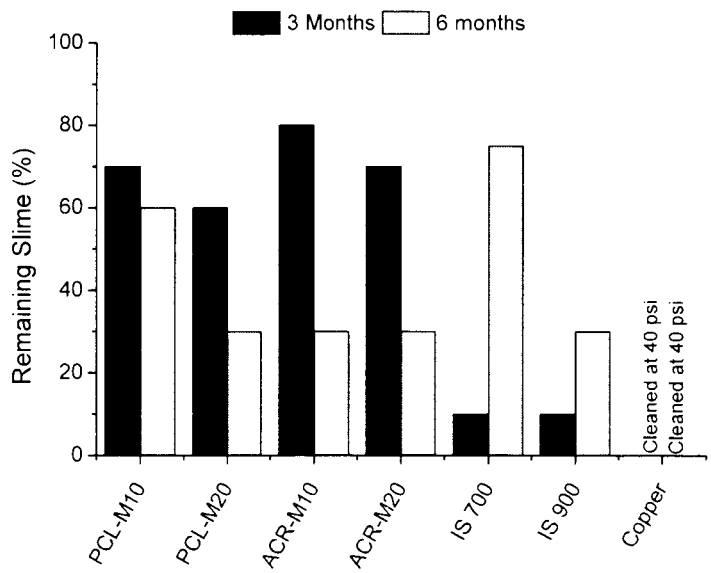

Figure 4.14. CalPoly water jetting of slime at 3 and 6 months of immersion on a single replicate panel.

The removal of hard fouling by water jet at Cal Poly is shown in Figure 4.15 at three and six months of immersion. The siloxane-polyurethane coatings required significantly higher water jet pressure to remove all of the fouling, and, as indicated by the data labels in Figure 4.15, the fouling was not 100% removed in all cases. The coatings prepared with 20% PDMS showed slightly lower amounts of hard fouling remaining after water jetting. While the high water jet pressures required for the removal of fouling compared to IS 700 and IS 900 shows that these coatings may not be as good for hard fouling removal, it should be noted that most of the fouling was removed (after six months of static immersion), even if a higher pressure was required.

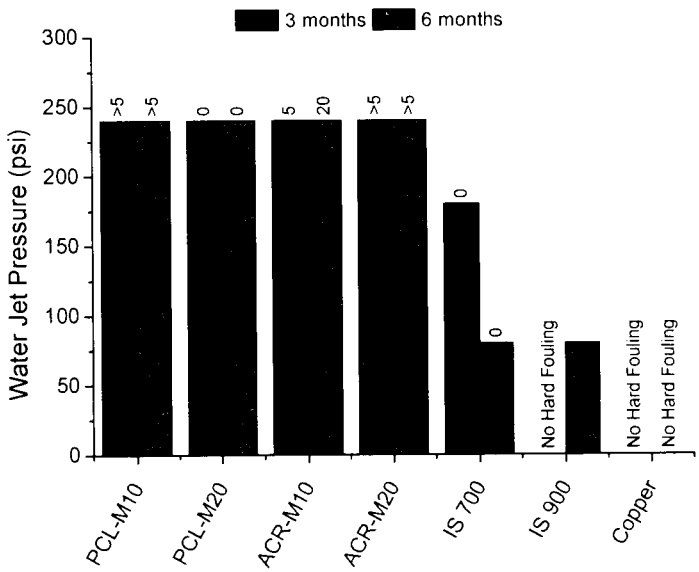

Figure 4.15. CalPoly water jetting of hard fouling at 3 and 6 months of immersion on a single replicate panel.

Barnacle adhesion strengths and the percentage of broken barnacles from lateral push-off measurements at CalPoly are shown in Figure 4.16. Coatings PCL-

M20 and ACR-M20 showed barnacle adhesion comparable to the IS 700 and IS 900 controls, and barnacle breakage was not observed for these coatings. Average barnacle adhesion on PCL-M10 was comparable to the FR controls, and only a small percentage of the barnacles tested were broken. Adhesion of barnacles on ACR-M10 was, on average, higher than on the other coatings and about 47% of the barnacle broke during testing. While even IS 700 showed 14% broken barnacles of those tested, this data shows that the coatings prepared with polycaprolactone polyol showed the best barnacle release at the CalPoly Morro Bay test site. The performance of three of the coatings was comparable to the FR controls in barnacle push-off, even though high water jet pressures were required for the removal of hard fouling. The barnacle adhesion shows that siloxane-polyurethane coatings can, in fact, provide release of barnacles in spite of the high water jetting required for their removal.

After 24 days of immersion at FIT, fouling consisted mostly of biofilms and soft fouling with some barnacles. The water jetting pressure to remove all of the fouling from a 1-1.5 in. diameter area on four panels is shown in Figure 4.17 where the data labels represent the number of panels cleaned completely for each sample. The siloxane-polyurethane coatings showed removal of fouling at water jet pressures comparable to those required to clean IS 700 and IS 900. Two and three panels of IS 700 and IS 900, respectively, cleaned with water jetting while all four panels of PCL-M10, PCL-M20, and ACR-M20 cleaned completely. Even though the values obtained for cleaning with water jet show overlap in standard deviations and are not statistically different, the ability to clean all four panels with water

jetting shows that these coatings offer good release of biofilms and soft fouling and the performance was comparable to IS 700 and IS 900.

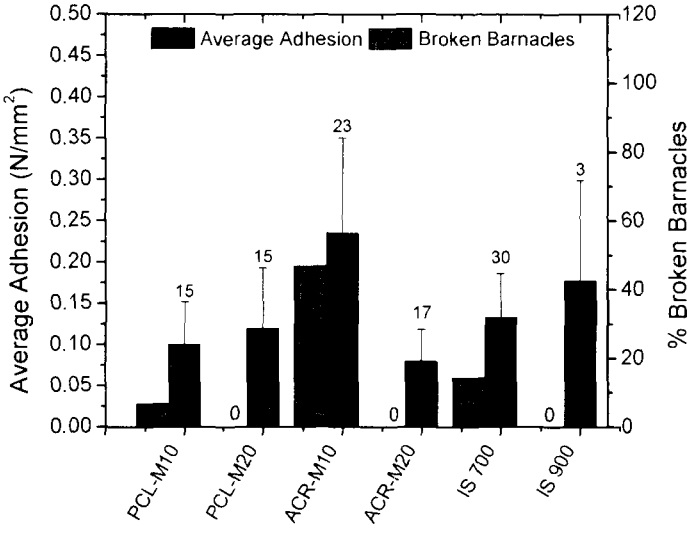

Figure 4.16. CalPoly barnacle removal force and broken barnacles observed in push-off testing. The values shown are the means of the number of measurements shown and the error bars represent one standard deviation of the mean.

After 76 days of immersion at FIT's Indian River Lagoon static immersion site, the fouling consisted of barnacles, tubeworms, and soft fouling and biofilm. Adult barnacles attached at this time and approximately 5 mm in diameter were tested in lateral barnacle push-off measurements. The results are shown in Figure 4.18. Barnacles on IS 900 were few and those attached were released during isolation preparation for testing. PCL-M20, ACR-M10, and ACR-M20 showed barnacle adhesion comparable to IS 700, in the range of 0.06-0.07 MPa. PCL-M10 showed slightly higher barnacle adhesion with an average value of 0.13 MPa.

Similar to barnacle push-off performed at CalPoly, the adhesion measurements at FIT show that the siloxane-polyurethane coatings offer comparable FR performance to the commercially available coating IS 700.

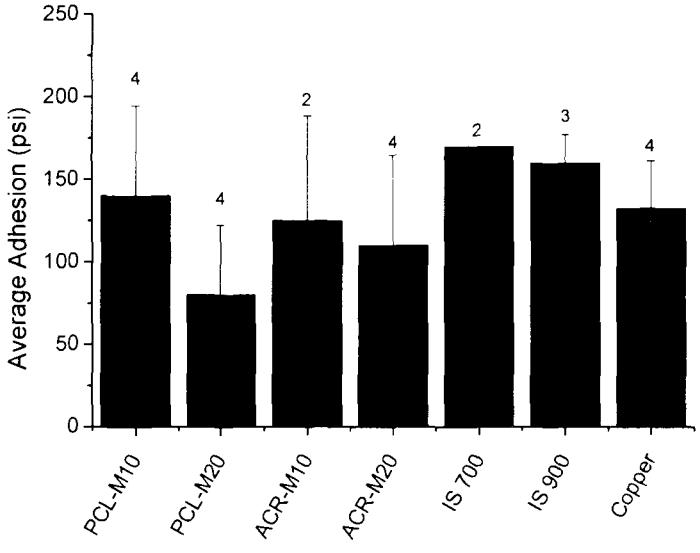

Figure 4.17. FIT water jetting after 24 days of immersion. The value is the mean pressure for 100% fouling removal from the number of replicates shown and the error bars represent one standard deviation of the mean.

Photos of panels immersed at The Republic of Singapore Yacht Club static immersion site for three months are shown in Figure 4.19 before and after soft sponging to remove fouling. The siloxane-polyurethane oatings prepared with acrylic polyol did not clean as well as those prepared with polycaprolactone polyol. This is evident when comparing PCL-M10 and ACR-M10 where ACR-M10 did not clean well with sponging and PCL-M10 was nearly completely cleaned following sponging. ACR-M20 also did not clean completely while PCL-M20 cleaned nearly 100% when sponged to remove fouling. Figure 4.20 shows photos of the coatings

before and after soft sponging at six months of immersion. IS 700 and IS 900 showed good cleaning ability, with almost complete removal of fouling with soft sponging. ACR-M20 showed fouling remaining after soft sponging, while PCL-M20 seemed to clean of most fouling. The same was true for PCL-M10 where most fouling was removed with sponging, with the exception of barnacles which were present in greater numbers than on PCL-M20. While soft sponging is less quantitative than the adhesion and water jetting measurements performed at CalPoly and FIT, the differentiation between coatings was shown quite nicely. Coatings prepared with PCL polyol showed better FR than those prepared with ACR polyol, and those prepared with 20% APT-PDMS-M showed better FR than those prepared with 10%.

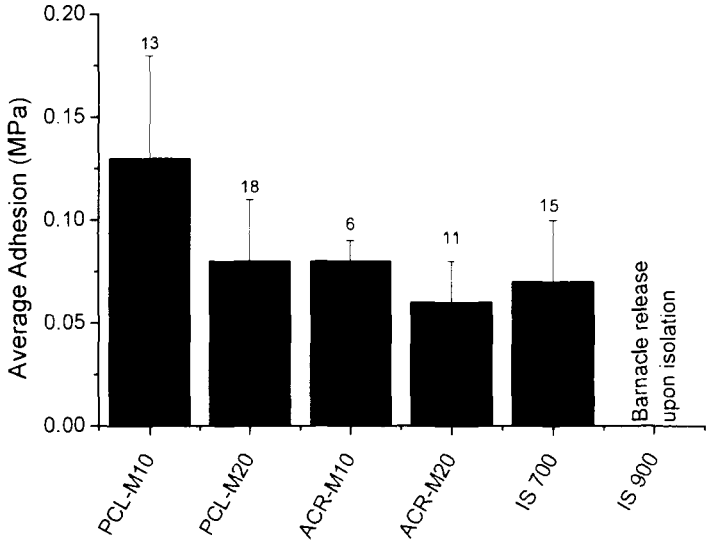

Figure 4.18 FIT barnacle adhesion after 76 days of immersion. The numbers of barnacles included in the data are shown as labels. The data are the means of these measurements and the error bars represent the standard deviation.

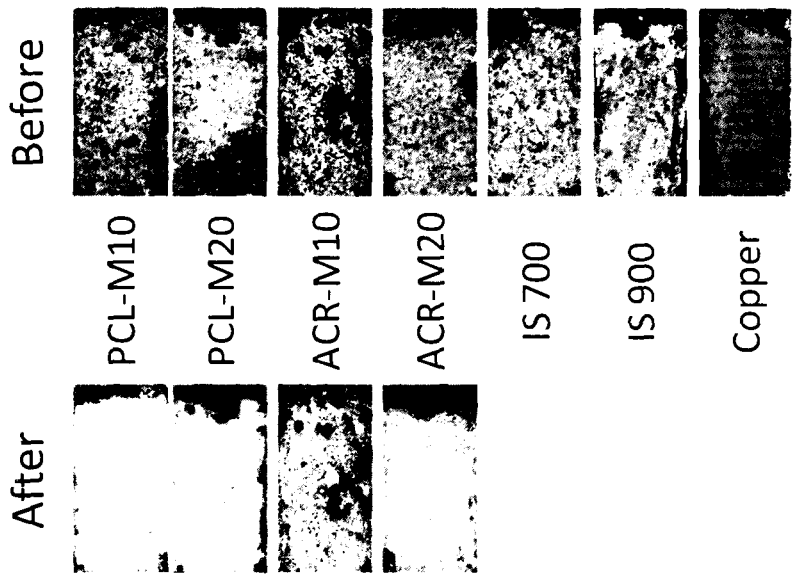

Figure 4.19 Panels before and after soft sponging at NUS, following three months of immersion.

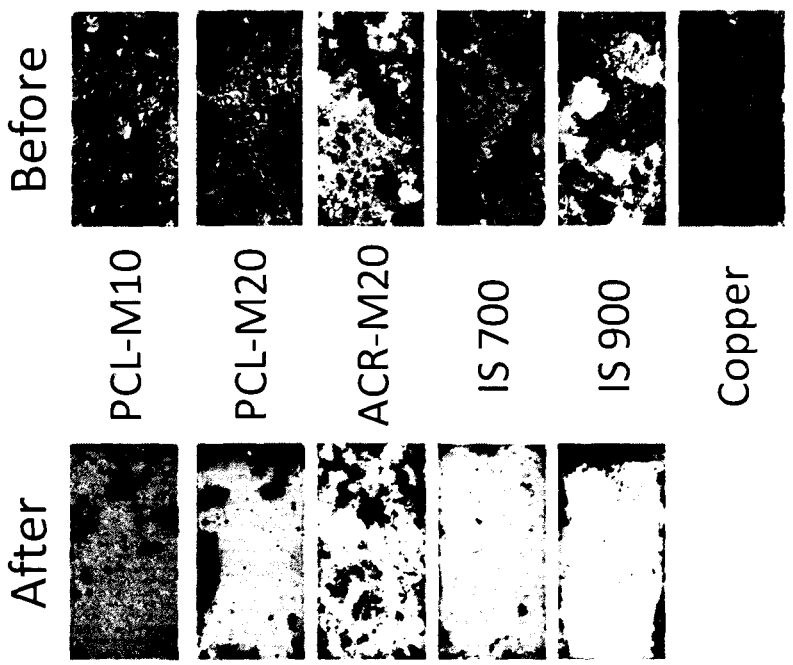

Figure 4.20. Panels before and after soft sponging at NUS, following six months of immersion.

4.4. Summary and conclusions

The work presented in this chapter was the culmination of polymer synthesis, coating preparation, and laboratory and field testing performed by many researchers at multiple sites in the world. Field testing is an important part of identifying top performing, new coating systems proposed for combating biofouling. However, field testing requires significant time and resources in determining the best performing coatings. Laboratory assays provide another method for prediction of fouling-release performance of new coating systems which requires a much shorter timeline for testing and significantly smaller coating amounts to perform the analysis.

The laboratory and field testing data in this chapter show the promise of siloxane-polyurethane coatings based on PDMS macromers in providing fouling-release performance. In the case of most lab and field tests, the siloxane-polyurethane fouling-release coatings were found to perform comparably to the commercially available fouling-release coatings, IS 700 and IS 900. However, IS 700 and IS 900 are elastomeric silicone coatings which are rubbery and mechanically weak. Additionally, they require a tie-coat to achieve satisfactory adhesion to marine primers. The siloxane-polyurethane coatings discussed here offer increased durability and adhesion to marine primers while maintaining the fouling-release performance that the currently commercially available fouling-release coatings offer. Therefore, these coating types are a welcome alternative to traditional fouling-release coatings due to their unique combination of toughness and durability with fouling-release performance.

4.5. References

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CHAPTER 5. UNDERWATER CLEANING TRIALS OF A SILOXANE-POLYURETHANE COATING PREPARED WITH AMINOPROPYL TERMINATED PDMS MACROMER

5.1. Introduction

Fouling of marine vessels incurs many costs and negatively affects the general performance of a vessel. One such issue is the operating speed, where a ship is forced to operate at a lower speed, or requires more power to operate at the same speed as a comparable vessel that is not fouled.[1] The hydrodynamic drag increase by the attachment of these organisms increases fuel consumption and reduces a ship's maneuverability.[2] Throughout history, humans have attempted to prevent extensive fouling of hulls through a variety of methods which have led to the variety of marine paints available on the market today.

Fouling-release (FR) coatings have been developed as non-toxic alternatives to antifouling (AF) coatings which have been found to have negative effects on non-target organisms.[3] Fouling-release coatings allow for fouling of their surface, but resist permanent attachment of the organisms and allow for their easy removal.[4] As potential replacements to these AF systems, an ideal situation would allow for the removal of fouling as a vessel moves through the water.[5] However, many vessels, especially naval vessels, may spend extended periods of time in port and can become so heavily fouled so that the complete removal of fouling by hydrodynamic flow becomes unrealistic and hull cleaning may be required to remove fouling.[5,6]

Antifouling hull coatings which have become heavily fouled require underwater cleaning to remove fouling before a ship leaves port. This process is considered essential, as it reduces fuel consumption by 15%, allows for a greater operating speed, extends the service life of paint, and helps maintain corrosion control.[7] With all of these benefits, hull cleaning costs considerably less than the increased fuel costs associated with a fouled hull.[8] Typically, heavy duty, self-propelled, diver maneuvered equipment is used to clean the surfaces of these paints. Using this type of equipment, it has been suggested that periodic hull cleaning of a hard, non-corrosive coating (without an AF or FR coating) could extend dry docking periods significantly.[3]

As interest in the development of FR coatings increases and a non-toxic alternative to poisonous AF paints becomes even more necessary, the performance of FR coatings is constantly questioned, as hull husbandry and the infrastructure it requires will inevitably face some level of change. Whether FR coatings can actually replace AF coatings and perform as required is constantly questioned. For instance, the accumulation of excessive fouling on these surfaces, could lead to increased fuel consumption and emissions,[9] thereby discrediting their existence as environmentally friendly paints. Therefore, as new FR coatings are developed, appropriate maintenance procedures, and schedules must be developed and tested to truly understand how the coating performance differs from the more traditional AF paints. This chapter addresses only a preliminary assessment where underwater cleaning of a siloxane-polyurethane FR coating was studied.

The objective of this work was to investigate the performance of a siloxane-polyurethane FR coating in an underwater cleaning study. Six tools were investigated for their removal of fouling from a single siloxane-polyurethane coating composition. The performance and durability of this coating was compared to the performance of a commercial FR coating for which the cleaning experiment was designed. The six tools consisted of heavy duty, brush cleaners of the type typically used in underwater hull cleaning, a hand held brush, a standard water jet, and a cavitating water jet. The removal of fouling from the coating surface and any damage incurred by the cleaning process was investigated and reported.

5.2. Experimental

5.2.1. Materials

Hexamethylcyclotrisiloxane (D_3) and dimethylchlorosilane (DMCS) were purchased from Gelest Inc. Inhibitor-free tetrahydrofuran (THF), acetylacetone (2,4-pentanedione, PD), lithium trimethylsilanolate (LTMS), allylamine, methyl amyl ketone (MAK), chloroplatinic acid hexahydrate, butyl acrylate, and hydroxylethyl acrylate were purchased from Sigma-Aldrich. Stabilized THF and toluene were received from VWR International. Desmodur® Z 4470 BA (IDT) was generously provided by Bayer MaterialScience and Vazo® 67 was generously provide by DuPont. Dibutyltin diacetate (DBTDAc) was supplied by Fluka. Intergard® 264 primer was received from International Paint and prepared according to manufacturer's specifications. Fiberglass/epoxy composite panels (10 in. x 12 in.) were received from Piedmont Plastics (G-10 Garolite Epoxy). A formed coating applicator rod (# 60) was received from Gardner.

5.2.2. Fiber glass panel preparation

Ten fiberglass panels were received and a single, 0.25 in. hole was drilled in each corner (1 in. from each edge). The panels were sanded in preparation for priming with the marine primer, Intergard 264. A powered pad sander was used to obtain satisfactory, uniform abrasion of the panels where circular, 100 grit sanding pads (3M Company) were used in a fume hood. Several sanding pads were used on each face of the panels until the surface was satisfactorily and uniformly roughened so that the original sheen of the panel was removed. The panels were rinsed with water to remove fine dust from the surface. Intergard 264 was applied via air-assisted spray application (70-80 μm coating thickness). One face was primed and allowed to ambient cure overnight. The following day, the opposite panel face was primed and the coating was ambient cured overnight. The siloxane-polyurethane coating was applied to one face of the panel three days after the priming was complete.

5.2.3. PDMS macromer polymerization

A similar preparation of PDMS macromer has been previously described.[10] A 50% mass solution of D_3 in inhibitor-free THF (504 g) was transferred to a 1000 ml RBF with activated molecular sieves (4.5 g). The solution was degassed by bubbling N_2 through it for 1 hr. The ring opening anionic polymerization was initiated by the addition of LTMS solution (10.7 g). The polymerization proceeded at room temperature for 3 hr with magnetic stirring, in a closed N_2 environment. DMCS (2.5 ml) was added to terminate the polymerization. The reaction mixture was magnetically stirred overnight at room temperature to allow for termination of

all polymer chains. The monohydride terminated PDMS macromer (HT-PDMS-M) was isolated by rotary evaporation and vacuum.

5.2.4. PDMS macromer functionalization

The functionalization of PDMS macromers with allylamine was described in Chapter 3. Hydrosilylation of allylamine with HT-PDMS-M was carried out to functionalize the PDMS macromer and yield monoamine terminated PDMS macromer (APT-PDMS-M). A solution of allylamine (4.5 g) and chloroplatinic acid hexahydrate (0.07 g) in inhibitor-free THF (18 g) was prepared in a 100 ml RBF. The orange solution was degassed by bubbling N_2 through it for 15 min and then heated to 60°C with magnetic stirring for 1 hr. The mixture was added to a 500 ml RBF with HT-PDMS-M (217 g). The reaction mixture was degassed by bubbling N_2 through it for 15 min at room temperature with magnetic stirring. The reaction mixture was heated at 90°C for 24 hr with magnetic stirring. The completion of the hydrosilylation reaction was determined by the absence of the silicon-hydride peak at 4.7 ppm in proton nuclear magnetic resonance spectroscopy (^{1}H-NMR). Following functionalization, the brown reaction mixture was rotary evaporated to remove excess allylamine and residual THF. The brown color was lessened by stirring in the presence of activated carbon.

5.2.5. Preparation of acrylic polyol

The preparation of a hydroxyl functional acrylic polymer was described in Chapter 4. The starved-feed free radical polymerization was performed in toluene in a 5000 ml reaction vessel. Toluene (960 g) was initially charged and heated to 80°C. A solution of monomer and initiator (butyl acrylate: 1200 g, hydroxyethyl

acrylate: 300 g, Vazo® 67: 60 g and toluene: 540 g) was added over approximately 3 hr at a feed rate of 12-13 ml min^{-1}. The reaction temperature was maintained in the range of 85-100°C. Following monomer/initiator addition, the reaction temperature was maintained for 30 min and a chaser solution of Vazo® 67 (6 g) in toluene (54 g) was added. The reaction temperature was maintained for one hour, and then cooled to room temperature with mechanical stirring. The final polymer was 50% solids in toluene.

5.2.6. Siloxane-polyurethane coating formulation, preparation and curing

The siloxane-polyurethane coating included in this study is the same in composition to ACR-M20 that was discussed in a previous chapter. The coating contains APT-PDMS-M (20.0%) which comprises the siloxane component, and IDT (32.3%) and acrylic polyol (47.7%) which comprise the polyurethane component. Formulation of the siloxane-polyurethane coating was carried out over two days. The APT-PDMS-M (40.0 g) and Desmodur (92.3 g) were added to a formulation vessel and mixed overnight by magnetic stirring at room temperature. The following day, a catalyst solution of DBTDAc (2.0 g, 5% in MAK) was added to the mixture, and it was stirred for 15 min. The PD (20.0 g) was added to the formulation, and it was shaken to mix. The acrylic polyol solution (190.8 g) was added, and the formulation was mixed by magnetic stirring at room temperature for 1 hr prior to coating application.

The siloxane-polyurethane coating was applied to ten fiber glass composite panels which had been previously primed with Intergard 264. Coating application was carried out using a formed applicator rod (Gardner, #60) in an attempt to coat

the entire width of the panel. Figure 5.1 shows two examples of the final primed and coated fiberglass panels. The coatings were ambient cured overnight and oven cured the following day at 80°C for 45 min. On all of the panels, there was some exposed primer. This was caused by coating formulation dripping through the holes which had been previously drilled in the panels, and due to not being able to start the application at the absolute top of the panel. For later testing and underwater cleaning, the most uniformly coated panels were placed in static immersion at Port Canaveral Air Force Base. These were not necessarily those which had the least amount of exposed primer. Therefore, varying amounts of exposed primer were present on the test panel edges, and this should be considered when examining photos where fouling has been cleaned from the panels using underwater cleaning devices.

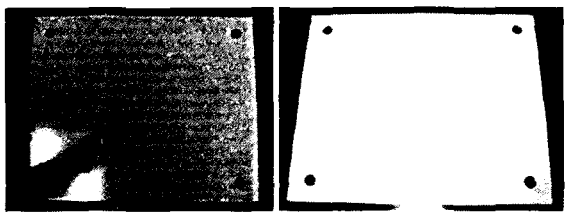

Figure 5.1. Fiberglass panels primed (Intergard 264) and coated with the siloxane-polyurethane coating ACR-M20.

5.2.7. Characterization of PDMS macromer and siloxane-polyurethane coating

5.2.7.1. Rapid® GPC: High-throughput gel permeation chromatography (GPC) was used to determine the approximate molecular weight of the PDMS and

acrylic polymers relative to polystyrene standards. The polymer solutions were prepared at a concentration of 2 mg ml^{-1} in stabilized THF prior to analysis. The analysis was performed using a Symyx® Rapid GPC with an evaporative light scattering detector (PL-ELS 1000), 2xPLgel Mixed-B columns (10 µm particle size) and a flow rate of 2.0 ml min^{-1}.

5.2.7.2. NMR Spectroscopy: Proton NMR (^{1}H-NMR) spectroscopy was performed using a Jeol 400 MHz spectrometer fixed with an autosampler. Solutions were prepared at 25 mg ml^{-1} in deuterated chloroform. Sixteen scans were performed with a 0.3 sec delay time.

5.2.7.3. Contact angle and surface energy: Contact angle and surface energy (SE) measurements were carried out using a Symyx® Coatings Surface Energy System with First Ten Ångstroms™ software. Three contact angles of water and methylene iodide were measured on the coating surfaces. A photograph was taken with a CCD camera, and automated image analysis was used to measure the wetting angle. The mean contact angles were used to calculate the surface energy of the coatings using the Owens-Wendt method.[11] This analysis was performed on fresh coatings (not immersed), and on panels that were cleaned three times with each SCAMP® E4 brush, hand brush, and Cavidyne.

5.2.8. Static immersion at Port Canaveral Air Force Base

Six panels were placed in static immersion at Poseidon Wharf, Port Canaveral, FL (28°24'38"N, 80°35'20"W), 25 days after coating application (December 2009). The panels were mounted beneath a floating raft on PVC racks using plastic fasteners. The raft rose and fell with the tide, so that the immersion

depth of the panels was kept constant. Three of the panels faced each north and south on the raft, and the same panel was always placed in the same spot on the raft and mounting rack. The static immersion area was caged by a net to prevent fish from entering and grazing on the fouled panels. Since the panels were very similar in appearance, they were marked with a uniquely colored plastic fastener. Figure 5.2 shows photos of the floating static immersion raft and a PVC rack on which the panels were mounted.

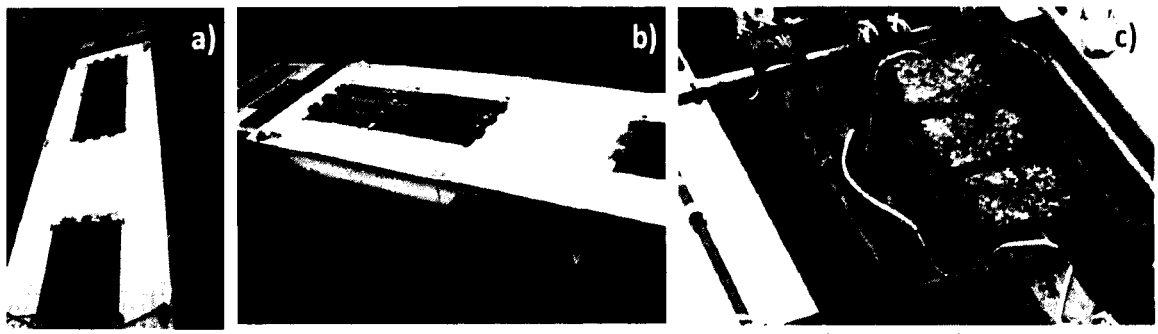

Figure 5.2. Static immersion under which test panels were immersed at a constant depth is shown in a) and b). c) shows the ACR-M20 panels on the PVC rack that was immersed below the raft.

5.2.9. Underwater cleaning apparatus and tools

The siloxane-polyurethane test panels were immersed and cleaned alongside a commercial FR coating (IS 900) to compare durability and FR performance. For cleaning, the fouled panels were removed from the static immersion raft and placed on a steel testing platform. During cleaning, the testing platform was mounted onto a steel testing frame affixed to the side of the wharf, underwater. This steel testing frame was placed in the water at the beginning of each cleaning trial, and removed on the final day of that trial. The steel testing

platforms were portable testing plates that were removed and placed in the water for cleaning with each tool. The steel testing platforms fit into gaps in the steel testing frame, resulting in a flat surface (flush with the testing frame) on which the cleaning tools could be run. Figure 5.3 shows the steel testing frame and Figure 5.4 shows the testing platform on which test panels were mounted.

Figure 5.3. Steel frame that was mounted to the side of the pier for testing. The testing platforms were mounted flush in the gaps. c) shows the testing frame being lifted into the water at the start of a cleaning trial.

Six unique cleaning tools were each used to clean one of the six panels immersed at Port Canaveral. The same tool was used to clean the same panel during each cleaning trial. Two diving companies provided and operated the cleaning tools for the cleaning trials. Seaward Marine Services (Norfolk, VA) operated the following tools: SCAMP® (E4 and E5 brushes), hand brush, and standard water jet. Oceaneering International, Inc. (Marine Services Division, Chesapeake, VA) operated the Cavidyne and Mini Pamper. When the large hull cleaning equipment was used (SCAMP® and Mini Pamper), a large (20 in. x 24 in.) fouling-entrainment panel was cleaned prior to cleaning the test panels. This was intended to increase the similarities of this small scale test with actual hull

cleaning, where a cleaning brush would have been used to clean other areas of a ship's hull prior to cleaning a test patch.

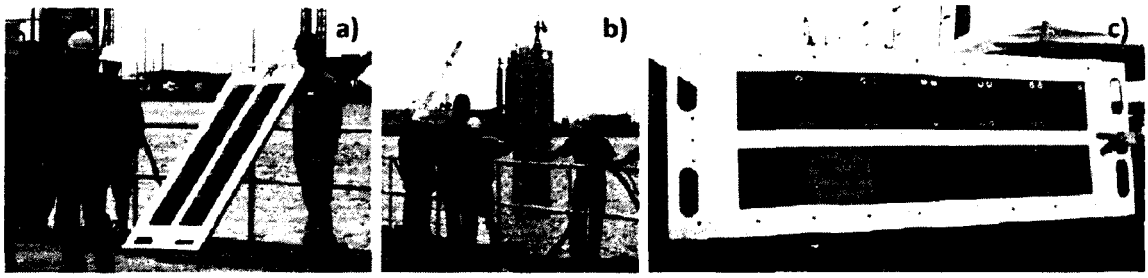

Figure 5.4. Testing platform on which test panels were mounted. a) and b) show the testing platform with fouled test panels and c) shows the testing platform with test panels which have been cleaned underwater.

The SCAMP® tool was a self-propelled, diver operated cleaning tool commonly used in underwater ship hull cleaning. The SCAMP® cleaning tool is pictured in Figure 5.5. This tool had three rotating brushes which had thick (approx. 3 mm diameter), stiff, nylon bristles. Two configurations of stiff nylon bristles on wooden platforms (E4 and E5) were used in cleaning the panels. Figure 5.6 shows the SCAMP® brushes, and the configuration of the bristles. The E5 brush had bristles which were slightly angled (in a sweeping arrangement) from the center of the brush and the E4 brush had bristles which extended straight out from the center of the brush. To flatten the edge of the bristles which contacted the test panels during cleaning, the SCAMP® was run on the concrete pier for approximately two minutes prior to being used to clean the panels. A schematic illustrating the flattening of the bristles is shown in Figure 5.7.

Figure 5.5. SCAMP® cleaning tool where a) shows the tool when stood on end b) shows the tool being run on the pier prior to use in panel cleaning, and c) shows the SCAMP® being maneuvered by a diver in Port Canaveral waters.

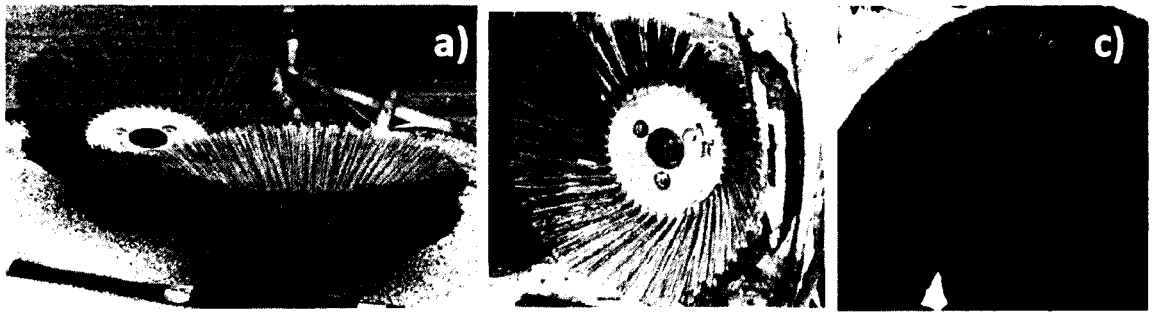

Figure 5.6. SCAMP® brushes where a) shows both the E5 (left) and the E4 (right) brushes, b) shows the E5 brush mounted on the SCAMP®, and c) shows the E4 brush mounted on the tool. As illustrated, the E5 bristles are angled slightly from the center of the brush while the E4 bristles extend straight out from the center mounting disk.

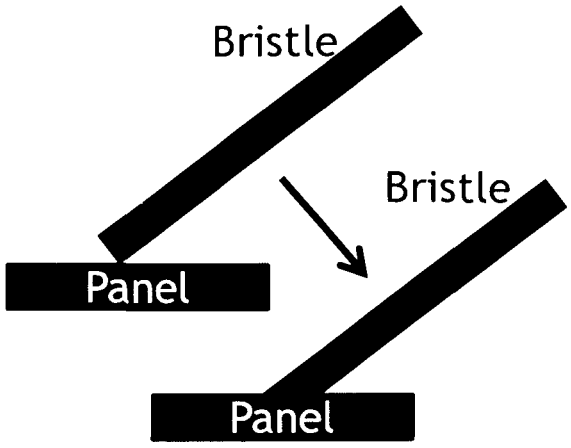

Figure 5.7. Flattening of SCAMP® bristles which occurred as the tool was run on the concrete pier prior to contact with test panel surfaces.

The hand brush was a small, hand held brush that contained bristles similar to those found on the SCAMP® E5 brush, but were shorter in length. This tool contained only one brush, and was also operated by a diver. Similar to the SCAMP® tools, the hand brush was also run on the concrete pier prior to coming into contact with the test surfaces. A photo of the hand brush is shown in Figure 5.8. The standard water jet (not pictured) was operated underwater by divers. The pressure was set to 2500 psi (without water resistance), and the jet was operated with approximately 6 in. of head space between the water jet and test panel.

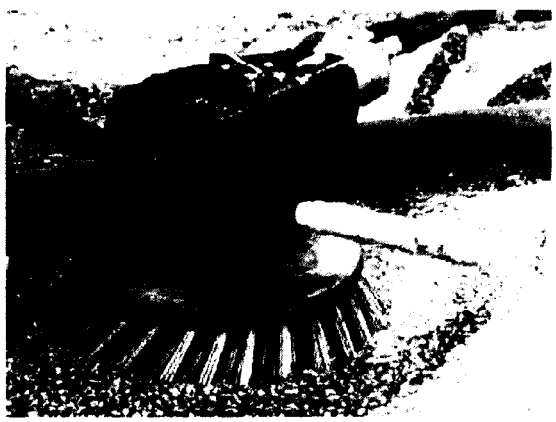

Figure 5.8. Hand held brush used to clean test panels, where the sweeping bristles resembled those of the SCAMP® E5 brush.

The Mini Pamper was a self-propelled tool that removed fouling using two rotating brushes. Unlike the other brush cleaning tools mentioned previously, the brushes on this tool had controllable depth, and their contact with test panels could be fine tuned. The bristles on the Mini Pamper brushes were arranged into linear segments and staggered around the circular base of the brush. As was done for the other brush tools, the bristles were flattened by running the Mini Pamper on the

concrete pier for approximately two minutes prior to testing. The Mini Pamper is pictured in Figure 5.9. The Cavidyne (not pictured) was a cavitating water jet that was operated by divers for underwater cleaning of fouled test panels. The Cavidyne was operated at 2000 psi which yielded approximately 1700 psi underwater. This pressure, along with cavitation, was used to remove fouling from the test panels.

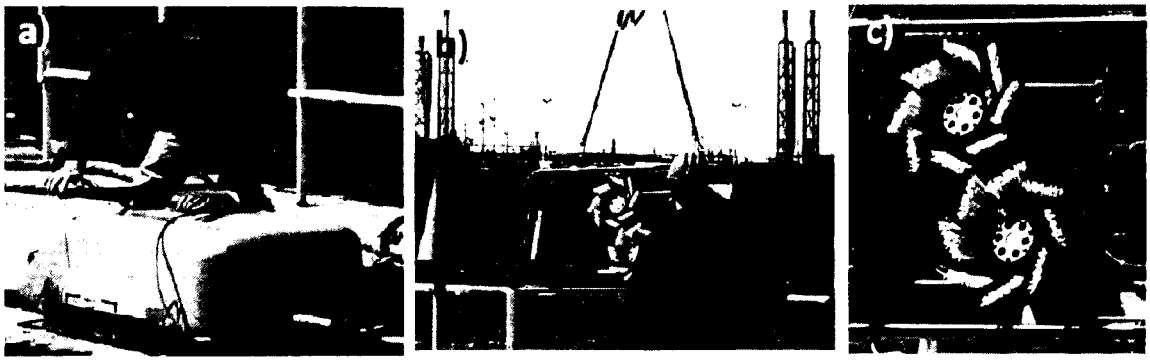

Figure 5.9. Mini Pamper cleaning tool where a) shows the Mini Pamper being run on the concrete to flatten the bristles prior to testing, b) shows the Mini Pamper being lifted into the water, and c) shows a close up of the bristle configuration for the Mini Pamper.

5.2.10. Underwater cleaning trials

5.2.10.1. February, 2010: The February, 2010 cleaning trial was held February 22-25, 2010. The siloxane-polyurethane coated test panels had been immersed on the static immersion raft for 53 days prior to this cleaning trial. Fouling at this time consisted mostly of biofilm and slimes. Small arborescent bryozoans (approximately 1 cm in height) were also widespread on the panels. Other fouling that was inconsistent on the panels included very small barnacles, small tube worms, and small encrusting bryozoans. After each panel was cleaned,

it was re-immersed on the static immersion raft at the same position as it was previously mounted.

5.2.10.2. June, 2010: The June, 2010 cleaning trial was held June 7-10, 2010. The siloxane-polyurethane coated test panels had been immersed on the static immersion raft for 102 days since last being cleaned in February, 2010. The fouling present on the panels before cleaning included tubeworms, tunicates (solitary and colonized), sponges, slime, occasional small barnacles, and arborescent and encrusting bryozoans. On one panel, flatworms were present, which are known predators of freshly settled barnacles. After each panel was cleaned, it was reimmersed on the static immersion raft at the same position as it was previously mounted.

5.2.10.3. September, 2010: The September, 2010 cleaning trial was held September 13-16, 2010. The siloxane-polyurethane coated test panels had been immersed on the static immersion raft for 94 days since last being cleaned in June, 2010. Fouling covered the entirety of the panels. The heavy fouling consisted of tubeworms, tunicates (solitary and colonized), sponges, slime, barnacles, multicellular algae, and bryozoans. After each panel was cleaned, it was reimmersed on the static immersion raft at the same position as it was previously mounted.

5.3. Results and discussion

5.3.1. Characterization of PDMS macromers

The results from the Rapid GPC characterization of the polymers used to prepare the siloxane-polyurethane coating are summarized in Table 5.1. The

molecular weight of the APT-PDMS-M was near the target molecular weight of 30,000 g/mol, and a narrow polydispersity index (PDI) was obtained. This illustrates the success of the anionic polymerization of which a narrow PDI and accurate target molecular weight are characteristic. Once the molecular weight was confirmed, macromer functionalization was carried out and coatings were prepared. The results of coating characterization will be discussed later in the chapter.

Table 5.1. Rapid GPC results for the characterization of the polymers used in the preparation of the siloxane-polyurethane coating ACR-M20.

Polymer	$\overline{M_n}$	$\overline{M_w}$	PDI
APT-PDMS-M	27,100	30,200	1.1
Acrylic Polyol	9,200	18,600	2.0

5.3.2. Cleaning trials

The test panel that was cleaned with the SCAMP® E4 brush is shown in Figure 5.10 where photos of the panel before and after cleaning in the February, June, and September cleaning trials are shown. Before cleaning during the February cleaning trial, the panel had a visible region along the edge of the panel where there was exposed primer. This region was no longer visible after the cleaning trial, illustrating that both the siloxane-polyurethane coating and the primer cleaned with the SCAMP® E4 brush at this time. In June, the panel was more heavily fouled than for the February cleaning trial. Following cleaning, the panel was completely cleaned, but fouling remained on the edges of the panel

where there was exposed primer. In the September cleaning trial, the panel was heavily fouled with barnacles and tubeworms. Most of the fouling was removed during cleaning, but some barnacles remained attached the panel. Biofilm and other fouling also remained, but this may have been because the bristles did not make full contact with the coating surface due to the barnacles remaining on the panel. Due to the barnacles remaining on the panels after cleaning, testing was discontinued on this panel beyond the September cleaning trial. The remaining barnacles were removed with a putty knife and a soft cloth was used to remove the remaining slime.

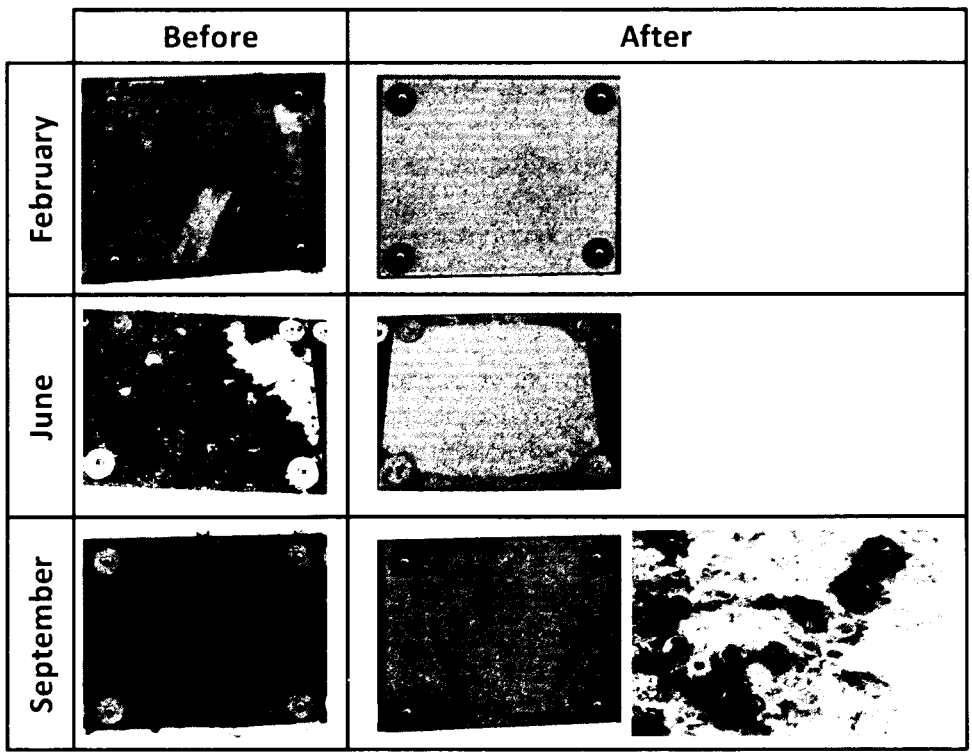

Figure 5.10. Siloxane-polyurethane test panels shown before and after cleaning with the SCAMP® E4 brush in February, June, and September of 2010.

During cleaning with the SCAMP® E4 brush, the siloxane-polyurethane coating showed only slight surface damage. After underwater cleaning with this tool at three cleaning trials, only superficial scratching was observed with the exception of one heavier scratch that could be felt by rubbing a finger on the coating surface. The damage incurred on this coating for this test was less than that observed for the commercial FR coating which showed significant coating degradation and scratching following multiple cleaning trials. However, the commercial FR coating showed complete cleaning at all of the trials, with the exception of tubeworm adhesive remaining after cleaning in February and June.

Photos of the test panel that was cleaned with the SCAMP® E5 brush at the February, June and September cleaning trials are shown in Figure 5.11. In the February and June cleaning trials, the panel cleaned completely with the E5 brush. However, a small section of the panel was missed during the June trial, as evidenced in the photo where the entire panel was clean and only a small section of fouling remained. This fouling was removed by gentle hand sweeping prior to placing the panel back on the static immersion rack. In the September cleaning trial, the test panel had many barnacles that remained dispersed on the panel following cleaning. Slime also remained in some spots on the panel, and this may have been due to the lack of brush-surface contact due to the barnacles present on the surface. Testing was discontinued beyond the September cleaning trial due to poor cleaning and lack of barnacle removal. The remaining barnacles and barnacle base plates were removed with a putty knife, and wiping with a soft cloth allowed for the removal of the slime.

The test panel cleaned with the SCAMP® E5 brush showed only surface scratching during cleaning, similar to the panel cleaned with the E4 brush. Again, the siloxane-polyurethane coating showed considerably less damage than the commercial FR coating also included in this test. However, the commercial FR coating showed complete cleaning at all of the trials, with the exception of tubeworm adhesive remaining after cleaning in February and June. It should be noted, however, that the siloxane-polyurethane coating showed excellent cleanability using the SCAMP® tool (both brushes) when lighter fouling had accumulated on the test panel. Since the fouling season is quite heavy during the summers in Florida, perhaps the siloxane-polyurethane coating would have shown better cleaning performance if it had been cleaned sooner, before the accumulation of such heavy fouling.

Figure 5.12 shows the photos taken of the test panel cleaned with the hand held brush in February, June, and September. This test panel was completely cleaned in the February and June cleaning trials. In the September cleaning trial, the panel was mostly cleaned, but some slime remained on the coating. A single barnacle (approximately 1 cm in diameter) remained on the edge of the panel, and several barnacle base plates were left behind by the brush. The slime that remained was mostly underneath barnacle base plates where it could not be reached by the brush. Coating scratching caused by the hand brush was more prevalent than scratching on the test panels cleaned by the SCAMP®. However, the scratching was only at the very surface of the coating, did not go through the coating to the primer, and less damage was caused to the siloxane-polyurethane

coating compared to the commercial FR coating that was tested in parallel. This tool may be an appropriate cleaning method for siloxane-polyurethane coatings, as it removed most of the fouling even after the panel became heavily fouled. If the panel had been cleaned with less fouling, it may have cleaned even better. For instance, if the panel had been cleaned before the attached barnacles had grown so large, they may have been removed by the hand brush without leaving base plates behind. Testing on this panel was discontinued due the remaining barnacle base plates. The base plates were removed with a putty knife to yield a clean panel with surface scratching.

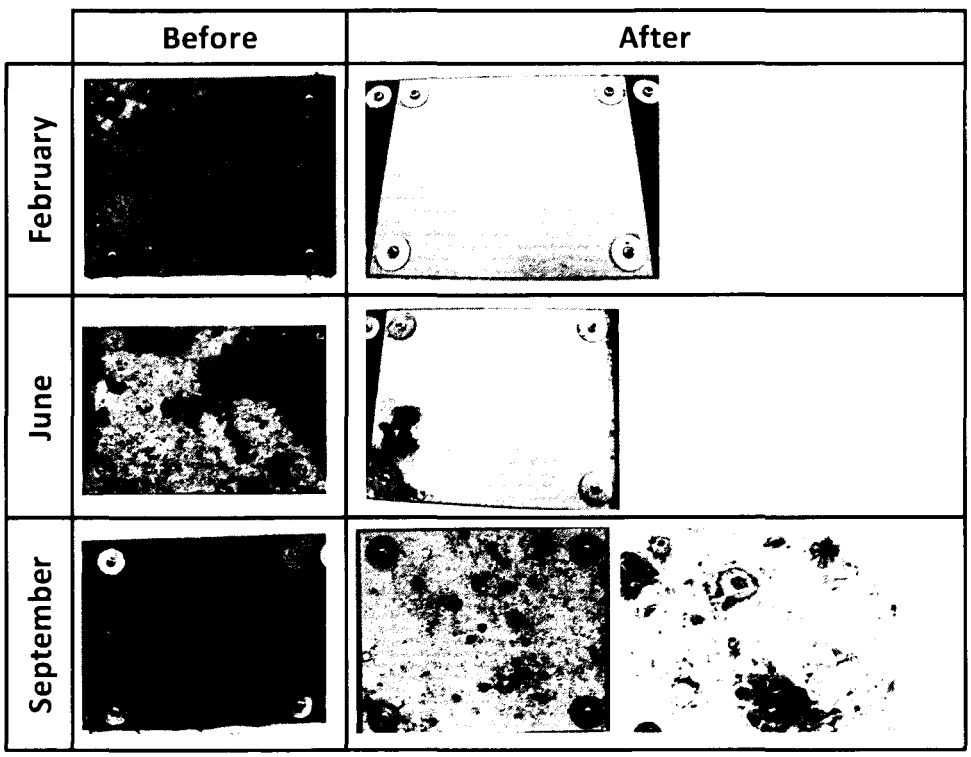

Figure 5.11. Siloxane-polyurethane test panels shown before and after cleaning with the SCAMP® E5 brush in February, June, and September of 2010.

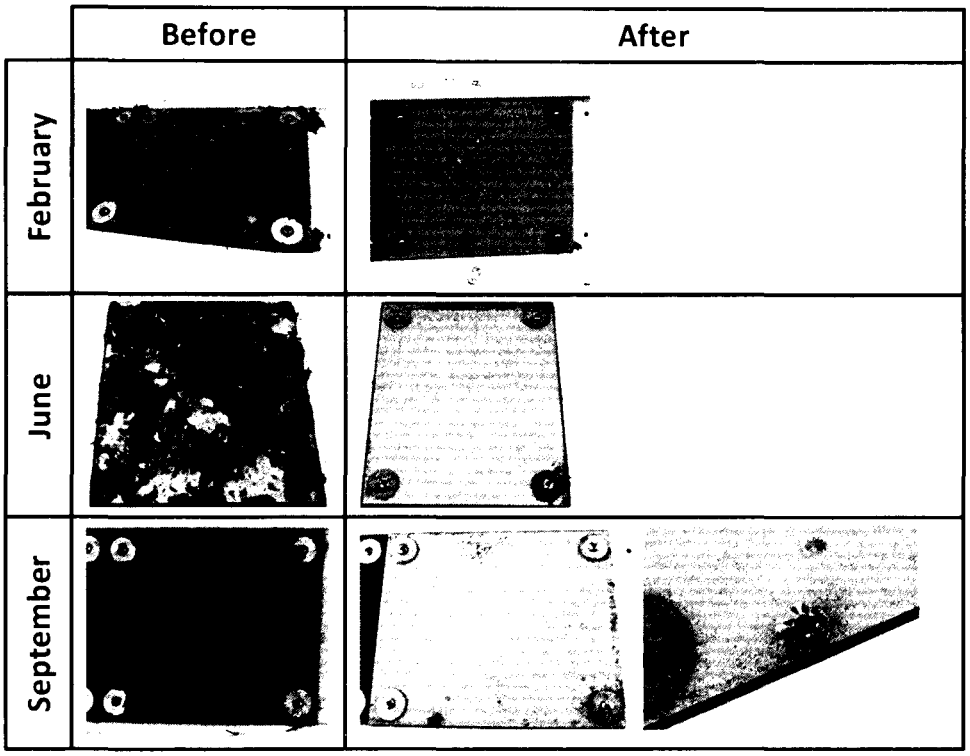

Figure 5.12. Siloxane-polyurethane test panels shown before and after cleaning with the hand brush in February, June, and September of 2010.

Photos of the test panel cleaned with the standard water jet during the February, June, and September cleaning trials are shown in Figure 5.13. As shown for the February, June and September cleaning trials, the ACR-M20 coating did not clean completely under water with the standard water jet. However, following underwater cleaning in February, the panel was cleaned with the same water jet pressure in air, and the surface was cleaned of fouling. In June and September, the panel did not clean underwater either. The panel was not cleaned in air with the water jet. In June, only slime remained on the test panel and it was immersed again with the remaining slime as shown in the photo after water jetting. In September, barnacles were removed from the test panel with underwater water jetting, and this was obvious on the test panel where regions of slime had been

removed with the barnacle. After water jetting, some barnacle base plates remained dispersed over the panel, in addition to the slime visible in the photo. Testing on this panel was discontinued after barnacle base plates were not removed in September with water jetting. The panel was cleaned with a cloth to remove the slime and the barnacle base plates were removed with a putty knife. There was no damage to the panel caused by cleaning with the water jet.

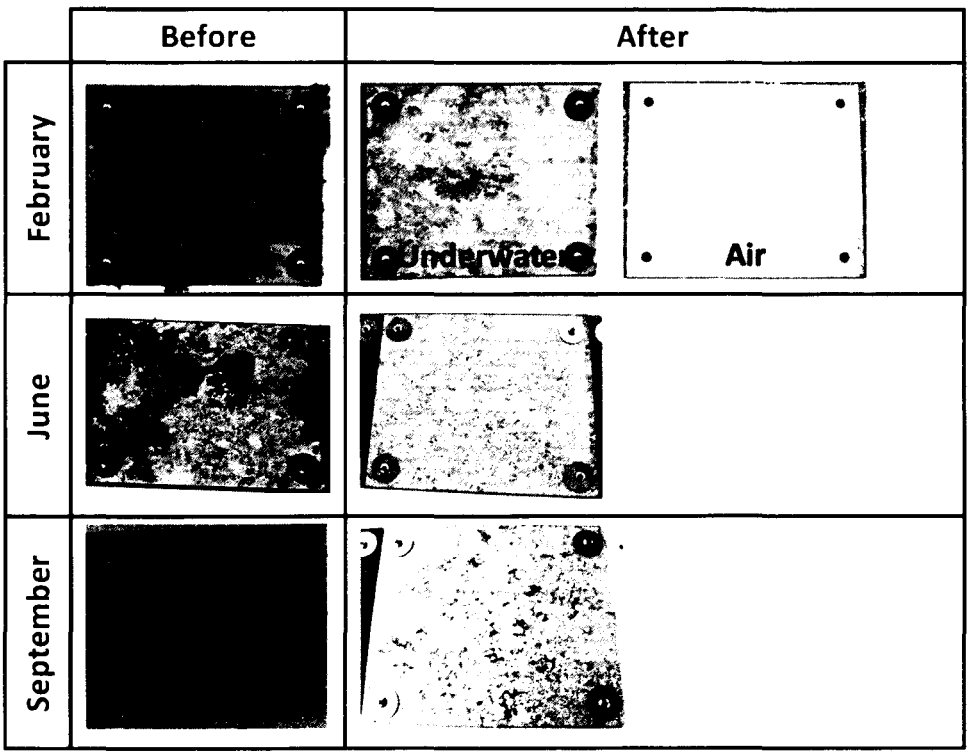

Figure 5.13. Siloxane-polyurethane test panels shown before and after cleaning with the standard water jet in February, June, and September of 2010.

In Figure 5.14, the photos of the test panel cleaned with the Mini Pamper in February, June, and September are shown. In the February cleaning trial, all of the fouling was removed from the ACR-M20 coating and only light surface scratching was observed. During the June cleaning trial, the surface seemed to have been

missed by the Mini Pamper where all of the macrofouling including tubeworms and tunicates were removed, but a slime layer remained. Other test panels of the commercial FR coating which were placed near the ACR-M20 panel also showed a remaining slime layer. However, the slime layer was easily wiped away with the rub of a finger. Therefore, the slime layer was cleaned from the panel using a soft cloth before being immersed again. In the September cleaning trial, the panel was mostly cleaned, but a few barnacles and barnacle base plates remained. Many surface scratches were observed over part of the panel where the Mini Pamper did not seem to have moved uniformly over the panel surface. However, these scratches were primarily surface scratches that could not be felt when a finger was rubbed on the surface. Testing was discontinued on this test panel due to the remaining barnacles and barnacle base plates. The barnacles and barnacle base plates were removed using a putty knife. A soft cloth was used to remove slime that remained on the panel.

The test panel cleaned with the Cavidyne is shown during the February, June, and September cleaning trials in Figure 5.15. During the February trial, the panel cleaned completely underwater. In the June cleaning trial, a slime layer remained on the panel after underwater cleaning. While the slime was easily removed by rubbing a finger on the coating surface, the panel was not cleaned prior to being placed back on the static immersion raft. After underwater cleaning with the Cavidyne in September, slime and barnacle base plates remained on the coating. Testing was discontinued on this test panel due to the barnacle base plates that could not be removed with the cleaning tool. The barnacle base plates

were removed with a putty knife and a soft cloth was used to wipe the slime away. The siloxane-polyurethane coating was damage-free except from some minor scratching from removal of the barnacle base plates.

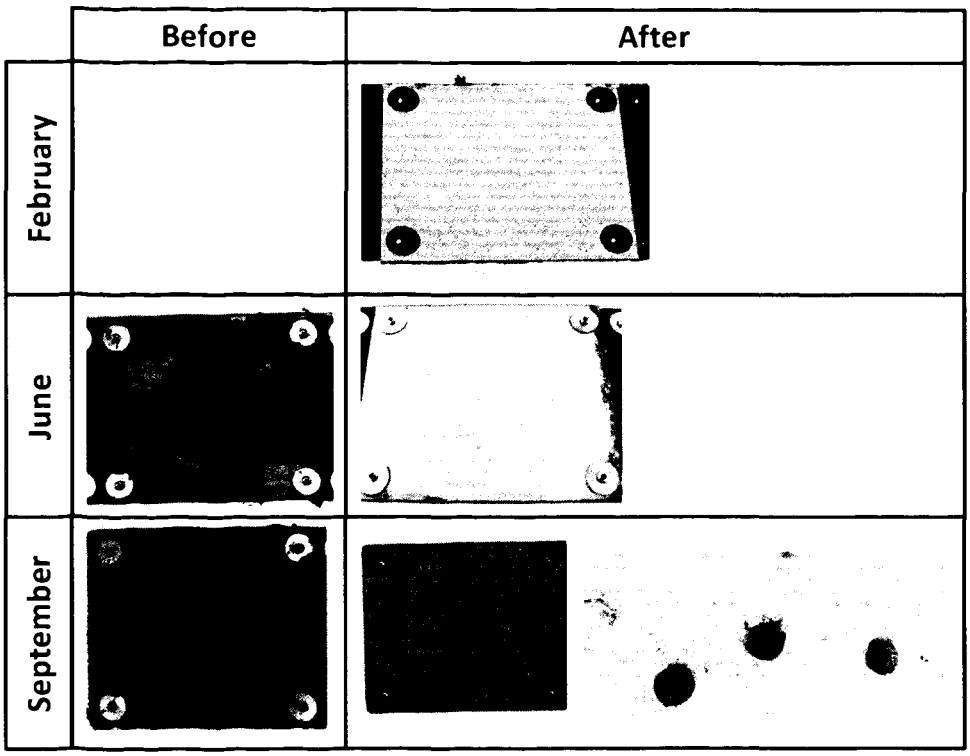

Figure 5.14. Siloxane-polyurethane test panels shown before and after cleaning with the Mini Pamper in February, June, and September of 2010.

After the test panels showed the inability to be cleaned during the September cleaning trial, the static immersion and underwater cleaning of these coatings was discontinued. The panels were cleaned of fouling that remained after underwater cleaning with the respective tools. Three test panels (SCAMP® E4 brush, hand brush, and Cavidyne) were sent to NDSU for surface analysis (water contact angle and surface energy) and three panels (SCAMP® E5, standard water jet, and Mini Pamper) were sent to a static immersion field testing site at Florida

the test panel which had not been immersed or cleaned (103°), and lowest for the panel which had been cleaned three times with the Cavidyne (94°). However, high WCA on all of the test panels demonstrated that the panels were still hydrophobic, indicating that PDMS was still present at the coating surface. Surface scratching may have been responsible for some lowering of the WCAs for these samples. While heavy scratching was avoided during the cleaning trials, some surface scratching did occur. Furthermore, the manual removal of barnacles and barnacle base plates following the September cleaning trial may have increased the surface scratching of these samples. The damage to the panel cleaned with the Cavidyne was minimal and limited to that caused by putty knife removal of barnacle base plates, but the surface may have still been contaminated with a film, resulting in the decrease in WCA.

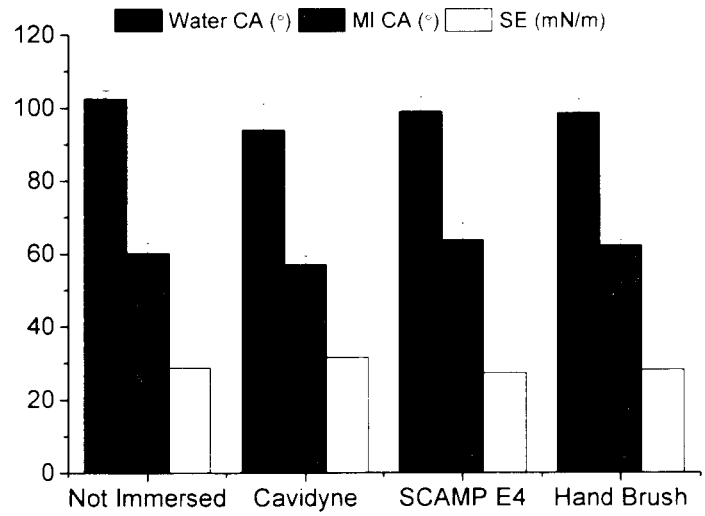

Figure 5.16. Water contact angle, methylene iodide contact angle, and surface energy of test panels where the contact angle values are the means of five measurements and the error bars represent one standard deviation of the mean.

5.4. Summary and conclusions

The underwater cleaning of siloxane-polyurethane FR coatings discussed here has demonstrated the potential of these coating systems to be effective FR coatings when subjected to routine cleaning with up to six months of immersion (December, 2009 to June, 2010). The performance of these coatings seemed to be depleted over time, leading to poor removal of barnacles in the September cleaning trial (9 months of immersion). With aggressive fouling in the Florida waters during the summer months, the panels had accumulated very heavy fouling that was to be removed in the September cleaning trial. Large barnacles up to 1 cm or more in diameter had grown on the panels, becoming difficult to remove. However, if the panels had been subjected to cleaning before fouling had become so extreme, the coating panels may have shown better cleaning in the September trial.

This cleaning study was designed to investigate the appropriate cleaning tools and conditions for the commercial FR coating, IS 900. However, this coating system is quite different than the siloxane-polyurethane coating discussed herein. While IS 900 is a soft, elastomeric coating, siloxane-polyurethane coatings are much harder and therefore may require a different cleaning tool or cleaning schedule to achieve the same performance. For instance, the IS 900 coating became heavily damaged with the brush cleaning tools, while the ACR-M20 coating was relatively undamaged. Perhaps the ACR-M20 coating could be exposed to a more aggressive brush cleaning tool to remove heavy fouling such as that which was present at the end of this study. Alternatively, the ACR-M20 coating

could likely stand up to more frequent cleaning with brush cleaning tools such as the SCAMP® or Mini Pamper. Further analysis would be required to assess the performance of these coatings when exposed to different tools or cleaning conditions. Because of the high investment for such experimentation, this will likely not occur. However, future "grooming" studies are expected where the coating surfaces will be exposed to more frequent (weekly) cleaning and the time where the coatings remain free of fouling will be studied.

5.5. References

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CHAPTER 6. EFFECTS OF PIGMENTATION ON SILOXANE-POLYURETHANE COATINGS AND THEIR PERFORMANCE AS FOULING-RELEASE MARINE COATINGS

6.1. Introduction

Marine biofouling refers to the settlement and buildup of marine organisms onto materials placed into natural waters.[1] More than 4000 organisms have been identified as marine biofoulers throughout the world. The accumulation of these organisms onto ships causes many problems such as reduced maneuverability and top operating speed,[2] up to a 40% increase in fuel consumption[3], increased frequency of dry docking,[1] paint or surface damage, and ecological introduction of non-native species.[4,5] These detrimental effects cost the US Navy an estimated $1 billion per year[6] and influence the shipping and cruise industries to an even greater extent.

An ancient problem, humans have developed and explored extensive methods for reducing or preventing biofouling.[7] Some of the early methods of combating biofouling on ships included lead and copper sheathing, and various compositions from an endless list of materials such as tar, wax, pitch, oil, resin, and tallow.[1] Coating development and ship manufacture from iron eventually led to the development of antifouling paints which are still in use today. The systems include active ingredients which prevent fouling from accumulating on a ship due to the toxic nature of the paints.[8] While these systems are effective in preventing and reducing biofouling on ships, they have received negative attention recently, as active ingredients can leach from the paints and negatively affect organisms that

reside in ports and shipyards.[4] This toxicity for non-target organisms and the current and future regulatory issues have increased the need for a non-toxic ship paint which effectively reduces biofouling.

Fouling-release (FR) coatings are another type of paint that can be used to combat biofouling on ships. Different from antifouling coatings, these systems are generally non-toxic and allow organism settlement, but act as release coatings to ease the removal of biofouling.[9] Typical commercially available FR coatings are based on silicone elastomers which have shown promise, but become easily damaged in the marine environment and require a tie coat for satisfactory adhesion to marine primers.[1] Recent research has opened up many new approaches to improving performance and durability of traditional FR coatings.

Siloxane-polyurethane coatings offer an advantage over traditional FR coatings because their composition can couple the toughness and durability of polyurethanes while maintaining FR performance through a siloxane-rich surface.[10] The self-stratified morphology of these systems occurs during film formation and creates a coating with a tough and durable polyurethane bulk and a low surface energy poly(dimethylsiloxane) (PDMS) surface.[11] Because the systems are crosslinked polyurethane coatings, this morphology is locked into place and cannot rearrange when immersed in water.[12] These systems have shown promise as FR coatings, often demonstrating performance comparable to commercially available FR coatings in laboratory marine bioassays used to evaluate FR performance.[13] Analysis of these systems to date has consisted only of clear coatings, while marine paints often contain pigment. Because siloxane-

polyurethane coatings rely on self-stratification for the migration of PDMS to the coating surface, it is important to understand the effect of pigmentation on the coating properties, as the inclusion of pigments can affect the diffusion of additives to the surface of coatings.[14]

In this work, siloxane-polyurethane coatings were prepared as pigmented and unpigmented films to determine the effect of pigmentation on coating properties and FR performance. Twelve coatings were prepared at 0, 20, and 30 pigment volume concentration (PVC) and 0, 10, 20, and 30% loadings of aminopropyl terminated (APT-PDMS) based on binder mass. The coatings were assessed for water contact angle (WCA), surface energy (SE), pseudobarnacle (PB) pull off adhesion, and gloss. Laboratory bioassays were used to screen the FR performance of the coatings using marine bacteria, microalgae, and live adult barnacles. Biofilm retention and removal of *Cellulophaga lytica* (*C. lytica*), a common marine biofouling bacterium, was measured to gauge bacterial settlement and removal from the coating surfaces.[15] The brown slime forming microalgae diatom, *Navicula incerta* (*N. incerta*), was used to screen the FR performance of the coatings due to the diatom's ability to form well adhered biofilms on FR surfaces.[16,17] A laboratory bioassay based on this organism was used to assess its attachment and removal from the surfaces of these coatings. *Amphibalanus amphitrite* (*A. amphitrite*), a species of barnacle, was used to assess FR performance in the laboratory by lateral push off following 14 days of reattachment.[18]

6.2. Experimental

6.2.1. Materials

Titanium dioxide (TiO_2) R-706 organically treated pigment and Vazo 67 (2,2'-Azobis(2-methylbutyronitrile)) were generously supplied by DuPont. Methylene iodide, acetyl acetone (2,4-Pentanedione, PD), butyl acrylate, hydroxyethyl acrylate, dibutyltin diacetate (DBTDAc) and benzyltrimethylammonium hydroxide solution (40% in methanol) were purchased from Sigma-Aldrich. Desmodur Z4470 BA (Isophorone diisocyanate trimer (IDT), 70% in butyl acetate) was generously provided by Bayer MaterialScience. Toluene and tetrahydrofuran were purchased from VWR International. Methyl amyl ketone was supplied by Eastman Chemical. Octamethylcyclotetrasiloxane (D_4) was purchased from Dow Chemical. Bis(3-aminopropyl)-tetramethyldisiloxane (BAPTMDS) was received from Gelest, Inc. The pigment dispersing aid Disperbyk-2150 was generously supplied by Byk-Chemie. All materials were used as received, without further purification.

Standard coating systems were prepared for comparative analysis in laboratory fouling-release bioassays. Intersleek® 700 (IS 700) and Intersleek® 900 (IS 900) were received from International Paint and prepared according to manufacturer's specifications. Silastic® T2 (T2) was received from Dow Corning, prepared according to their specifications and thinned with methyl isobutyl ketone. A polyurethane control coating (PU) was prepared with a 1.1 to 1 stoichiometric ratio of isocyanate to alcohol functional groups where the isocyanate resin was IDT

and the polyol was a polycaprolactone triol (Capa® 3050) supplied generously by Perstorp.

The marine bacterium *C. lytica* was generously provided by Dr. Michael Hadfield of the Kewalo Marine Laboratory, University of Hawaii. The marine diatom *N. incerta* was generously provided by Dr. Maureen Callow of the University of Birmingham, UK. Artificial seawater (ASW) was prepared by dissolving 38.5g of sea salts (Sigma-Aldrich) into 1L of deionized water. Bacterial biofilm growth medium (BGM) consisted of 0.1g yeast extract and 0.5g of peptone per 1L of ASW. Algal growth medium (F/2) consisted of 1L of ASW supplemented with nutrients to generate Guillard's F/2 medium.[17] BGM, F/2 and ASW were filter sterilized with 0.2 micron vacuum-cap filters. Crystal violet powder, 33% glacial acetic acid and dimethyl sulfoxide (DMSO) were used as received (VWR International).

6.2.2. Acrylic polyol preparation

A hydroxyl functional acrylic polymer was prepared using a starved-feed polymerization method in toluene. A 5000 mL four-neck flask was fitted with a condenser, overhead mechanical stirrer, nitrogen inlet and thermocouple, and a monomer pumping inlet. The flask was initially charged with toluene which was heated to 80°C. A monomer mixture of butyl acrylate (1200 g) and hydroxyethyl acrylate (300 g) was prepared in advance and mixed with an initiator solution of Vazo 67 (60 g) and toluene (540 g) immediately prior to use. The monomer and initiator addition was carried out with a feed rate of 12-13 mL min^{-1}, taking approximately three hours. During the monomer/initiator addition, the temperature

was maintained at 90-100°C. Following three hours of monomer addition, the reaction temperature was maintained at 95°C for 30 minutes. A chaser solution of Vazo 67 (6 g) and toluene (54 g) was added to the reaction mixture, and the temperature was maintained for one hour. The reactor was then removed from the heat source and cooled to room temperature while mechanical stirring was continued. The final concentration of the polyol was 50% by mass in toluene. The resulting polymer was characterized for percent solids and percent conversion in accordance with ASTM D2369.

6.2.3. Difunctional PDMS preparation

Siloxane monomer, D_4 (300 g), and benzyltrimethylammonium hydroxide solution (24.1 g) were added to a single neck 500 mL round bottom flask and methanol was removed using rotary evaporation. The resulting mixture was added to additional D_4 (9200 g) and BAPTDMS (80.27 g) in a 12 L, four neck round bottom flask equipped with an overhead stirrer, nitrogen inlet, condenser, heating mantle, and temperature controller. The monomer (D_4) and end blocker (BAPTDMS) were equilibrated for 24 hrs at 80 °C in a nitrogen environment.[19] After this time, the temperature was increased to 170 °C and held for 2 h to decompose the catalyst (benzyltrimethylammonium hydroxide). The reaction mixture was cooled to room temperature and stored.

6.2.4. Characterization of acrylic polyol and difunctional PDMS

6.2.4.1. Symyx Rapid® GPC: High-throughput gel permeation chromatography (GPC) was used to determine the approximate molecular weight of the PDMS and acrylic polymers relative to polystyrene standards. The polymer

solutions were prepared at a concentration of 2 mg mL^{-1} in stabilized THF prior to analysis. The analysis was performed using a Symyx® Rapid GPC with an evaporative light scattering detector (PL-ELS 1000), 2xPLgel Mixed-B columns (10 μm particle size) and a flow rate of 2.0 mL min^{-1}.

6.2.5. Pigment grind preparation

Pigment grinds were prepared by dispersing TiO_2 in the acrylic polyol. The acrylic polyol and pigment dispersant were combined in a steel beaker, and stirred to mix using a high speed disperser affixed with a Cowles blade. The pigment dispersant, Disperbyk-2150, was added so that a final concentration of 4% weight based on TiO_2 was achieved. The disperser speed was increased until an appropriate "doughnut" shape was obtained. The liquid formed a moving circle in the steel beaker where it was pulled (by the disperser blade) into the center, and drawn upward at the outside of the beaker.[20] Table 6.1 summarizes the pigment dispersions, or grinds, that were prepared and used in the preparation of pigmented siloxane-polyurethane coating formulations. In some cases, grind viscosity became extremely high during pigment dispersion, and toluene was added to help maintain an appropriate viscosity. Fineness of dispersion and Hegman values of the pigment grinds were determined in accordance with ASTM D1210.

6.2.6. Pigmented siloxane-polyurethane coating formulation

Siloxane-polyurethane coatings were formulated from the pigment grinds (acrylic polyol and TiO_2), IDT, APT-PDMS, DBTDAc catalyst solution, and PD as a pot-life extender. The ingredients used are summarized in Table 6.2. After the

siloxane-polyurethane coatings were prepared using a drawdown bar with an 8 mil gap thickness. Siloxane-polyurethane and polyurethane coatings were ambient cured overnight and force cured at 80°C for 45 min the following day. Commercial fouling-release coatings were cured under the same ambient conditions for at least 24 hrs prior to analysis. Table 6.3 summarizes the solid composition of the coatings.

Table 6.2. Materials and amounts used for the preparation of experimental siloxane-polyurethane FR coatings at 0, 20, and 30 PVC with 0, 10, 20, and 30% PDMS binder loading.

Coating ID	Grind #	Grind (g)	Polyol (g)	APT-PDMS (g)	Desmodur Z 4470 BA (g)	PD (g)	DBTDAc Solution (g)
0 PVC, 0% PDMS	NA	0.00	18.00	0.00	8.57	2.67	0.15
0 PVC, 10% PDMS	NA	0.00	21.54	2.00	10.33	2.00	0.16
0 PVC, 20% PDMS	NA	0.00	19.08	4.00	9.23	2.00	0.16
0 PVC, 30% PDMS	NA	0.00	16.62	8.00	8.13	2.00	0.16
20 PVC, 0% PDMS	1	27.00	3.10	0.00	8.91	3.14	0.15
20 PVC, 10% PDMS	1	25.35	0.30	1.40	7.42	3.05	0.15
20 PVC, 20% PDMS	3	23.00	1.00	2.70	6.16	2.97	0.15
20 PVC, 30% PDMS	2	21.70	2.00	4.50	5.81	2.88	0.15
30 PVC, 0% PDMS	2	33.00	2.00	0.00	8.00	3.14	0.15
30 PVC, 10% PDMS	2	34.21	0.00	1.40	7.22	3.05	0.15
30 PVC, 20% PDMS	4	33.80	0.00	2.90	7.01	2.97	0.15
30 PVC, 30% PDMS	5	39.00	0.00	4.80	6.81	2.88	0.15

Table 6.3. Composition of solid films formulated at 0, 20 and 30 PVC with 0, 10, 20, and 30% PDMS binder loading.

	Mass % Solids			
Coating ID	TiO_2	Acrylic Polyol	IDT	PDMS
0 PVC, 0% PDMS	0.00%	60.00%	40.00%	0.00%
0 PVC, 10% PDMS	0.00%	53.85%	36.15%	10.00%
0 PVC, 20% PDMS	0.00%	47.70%	32.30%	20.00%
0 PVC, 30% PDMS	0.00%	37.77%	25.87%	36.36%
20 PVC, 0% PDMS	45.91%	32.96%	21.13%	0.00%
20 PVC, 10% PDMS	47.04%	28.60%	19.19%	5.18%
20 PVC, 20% PDMS	48.53%	24.36%	16.67%	10.44%
20 PVC, 30% PDMS	48.81%	20.76%	14.45%	15.98%
30 PVC, 0% PDMS	60.01%	23.91%	16.08%	0.00%
30 PVC, 10% PDMS	60.79%	21.11%	14.17%	3.93%
30 PVC, 20% PDMS	60.96%	18.40%	12.97%	7.67%
30 PVC, 30% PDMS	61.14%	16.38%	11.20%	11.29%

6.2.8. Characterization of pigmented siloxane-polyurethane coating properties

6.2.8.1. Contact angle and surface energy analysis: Contact angle and SE characterization was performed using a Symyx®/First Ten Ångstroms™ Coating Surface Energy System. Three contact angles of each water and methylene iodide were measured and analyzed using the FTA software. The average water contact angle (WCA) and methylene iodide contact angle (MICA) were used to calculate the surface energy of the films, using the Owens-Wendt method.[21]

6.2.8.2. Gloss: Gloss measurements were obtained using a Byk-Gardner micro-TRI-gloss gloss meter. Three measurements were taken. The mean and standard deviation of these measurements were recorded.

6.2.8.3. Pseudobarnacle adhesion: Pseudobarnacle (PB) adhesion measurements were performed using a Symyx® Automated Pull-Off Adhesion System where the removal force of an aluminum stud (pseudobarnacle) to the

surface of a coating was measured.[22] The coated panels were placed on a vacuum plate which held them in place. A plastic template with 24 patches of three circular holes (7 mm diameter) was placed over the panels. A two-component epoxy adhesive (Loctite® Hysol® 1C-LV) was spread over the plastic template, depositing epoxy adhesive onto the coating. The plastic template was removed, leaving regions of adhesive behind, and the panels were placed into clamping jigs. Six PBs were applied per coating, and weighted foam blocks were placed over the studs for overnight curing. The following day, the foam blocks were removed, and the clamping jigs (with panels enclosed) were placed into the automated adhesion system. An automated pull-off head removed the pseudobarnacles by applying gradual force. The force at release was recorded for all measurements and a mean and standard deviation were calculated.

6.2.9. Characterization of pigmented siloxane-polyurethane fouling-release performance via laboratory assays

6.2.9.1. Coating pre-leaching and leachate toxicity analysis: All of the coatings were pre-leached in a recirculating clean water tank for four weeks prior to analysis with biological organisms to allow any toxic leachates which may have been present to be removed from the coatings. Following this pre-leaching period, the coatings were analyzed for leachate toxicity.[23] Extractions from each coating were performed by adding ASW and nutrients to wells of 24-well plates which contained coating samples. Growth of bacteria and microalgae in the extraction liquid was monitored after 24 hrs, by staining with crystal violet. The stain was then extracted and quantified by absorbance measurements at 600 nm. Growth of the

microalgae diatom was quantified by fluorescence measurement of chlorophyll (excitation wavelength: 360 nm, emission wavelength: 670 nm). Comparison with standard coatings and negative growth controls was used to determine that the coatings did not contain toxic leachates and biological analysis could be continued.

6.2.9.2. C. lytica *biofilm retention and adhesion:* High-throughput assessment of bacterial biofilm retention on coatings prepared in 24-well plates has been described previously.[23-25] The wells of the coating array plates were inoculated with 1.0 mL of *C. lytica* suspension (10^7 cells mL^{-1}) in BGM. The plates were incubated at 28°C for 24 h. The growth media and planktonic growth were discarded after incubation was complete and the coatings were rinsed three times with ASW to remove unattached or weakly adhered biofilm. The retained biofilms were dried for 1h under ambient conditions, and stained with crystal violet (0.3% w/v in deionized water). Extraction of the crystal violet stain from the biofilm was performed with 0.5 mL of 33% glacial acetic acid and the resulting eluates were measured for absorbance at 600 nm. A total of three replicate wells were measured. The absorbance values were considered to be directly proportional to the amount of biofilm retained on the coating surfaces.

The FR performance of the coatings with respect to *C. lytica* was characterized by exposing the attached biofilms to a pressurized jet of water using an automated device.[26] Four wells were inoculated with *C. lytica* culture and incubated as described above. Following incubation, the growth media and planktonic growth were discarded and the plates were rinsed three times with ASW to remove unattached cells, or weakly adhered biofilm. Three wells were water

jetted with a rotating water jet at 10 psi for 5 sec and three wells were left untreated to account for the initial biofilm retained on the coating surfaces. The remaining biofilm was stained with crystal violet which was extracted and used to quantify the accumulated biomass as described above.

6.2.9.3. N. incerta *attachment and adhesion:* The *N. incerta* cell adhesion assay was carried out in a similar manner to that described for the *C. lytica* biofilm retention and removal assays.[19,27,28] Coatings that were prepared in 24-well plates were inoculated with 1.0 mL of a suspension of *N. incerta* (10^5 cells mL^{-1}) in F/2. The plates were incubated for 2 h under ambient conditions. Following incubation, the plates were treated with the rotating water jet. Eight replicate wells were prepared for each coating system. Four replicates were water jetted at 10 psi for 10 sec and four replicates were left untreated to be measured as the initial attachment to the coatings. The plates were incubated in darkness for 30 min with 0.5 mL of DMSO in each well. Gentle agitation yielded a homogeneous solution of which 0.2 mL was transferred to a 96-well plate for fluorescence measurements of chlorophyll using a multi-well plate spectrophotometer (excitation wavelength: 360 nm, emission wavelength: 670 nm). The percent removal was recorded as the difference in relative fluorescence units (RFU) between the coating replicates that were exposed to the water jet and those left unexposed.

6.2.9.4. Adult barnacle reattachment: An adult barnacle reattachment assay was utilized to gauge the fouling-release performance of the coatings with respect to shell fouling.[18,29,30] Adult barnacles (*Amphibalanus amphitrite*) with a basal diameter of approximately 5 mm were removed from a silicone substrate and

placed on the coating panels. Nine barnacles were used for testing each coating. The barnacles were allowed to reattach to the coating surfaces by immersing the panels in an ASW aquarium system for 14 days with daily feedings of brine shrimp nauplii. The reattached barnacles were dislodged from the coating surfaces using a hand held digital force gauge in accordance with ASTM D5618. A digital force gauge was placed at the barnacle base plate, parallel to the coating surface, and pushed laterally (in shear) until it became detached from the surface. Once detached, the areas of the barnacle base plates were measured using image analysis (Sigma Scan Pro5.0). Barnacle adhesion strengths were calculated from the removal force and the area of the barnacle base plates. The adhesion values for each coating were reported as the mean of the total number of barnacles exhibiting a measurable removal force. During testing of well adhered barnacles, the organism's shell sometimes broke before the barnacle was dislodged from the coating. In these cases, the removal force was not included in the calculation of the mean, and the number of broken barnacles was recorded as part of the measurement.

6.3. Results and discussion

The results from characterization of the acrylic and polysiloxane polymers used in the coatings are shown in Table 6.4. The GPC results show that the molecular weight of the APT-PDMS was near the targeted value of 30,000 g/mol. Additionally, the molecular weight of the acrylic polyol and the equivalent weight shows that each polymer chain of acrylic polyol, on average, would have multiple hydroxyl groups, since the conversion of monomer to polymer was 100%.

Table 6.4. Polymer characterization including GPC and percent conversion for the acrylic polyol and APT-PDMS.

Sample	$\overline{M_n}$	$\overline{M_w}$	PDI	% Conversion	Equivalent Weight (g/equiv.)
APT-PDMS	27,000	40,500	1.5	NM	15,000 (NH_2)
Acrylic Polyol	6200	13,100	2.1	100%	580 (OH)

NM: Not measured

Figures 6.1 and 6.2 show the WCA and SE of the cured, experimental films. Figure 6.1 shows that the inclusion of 10, 20, and 30% PDMS caused an increase in WCA. For the 0 PVC coatings, the WCA for all of the coatings were near 105°. The WCA of the pigmented systems (20 and 30 PVC) increased with an increase in PDMS content, to a maximum value near 105°. This illustrates that the WCA and surface hydrophobicity of the films was affected by pigmentation of the coatings, where a WCA near 105° was observed only when a higher loading of PDMS was used. The 0 PVC coatings showed a WCA of near 105° when only 10% PDMS loading was used whereas the pigmented coatings required 20-30% PDMS for the same result. The coatings containing PDMS showed a great reduction of SE from the pure polyurethane samples, as shown in Figure 6.2. All of the polyurethane (0% PDMS) samples had SE of approximately 35 mN/m whereas the SE for the samples containing PDMS was significantly lower and resembled that of pure PDMS. The SE and WCA data show that the PDMS in the experimental coatings has stratified to the surface of the films, due to the comparatively low SE of the PDMS compared to the polyurethane bulk. However, the marked increase in WCA for 0 PVC coatings containing only 10% PDMS was not reflected as strongly in the pigmented coatings, suggesting that pigmentation

had slightly affected the migration of PDMS to the coating surface during film formation.

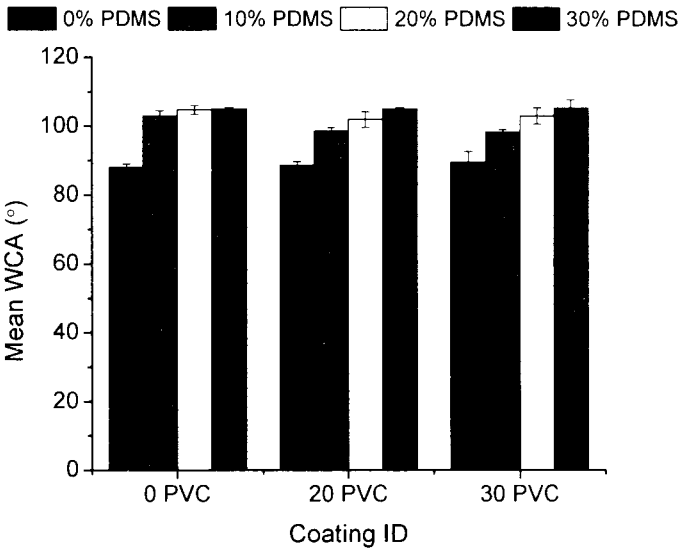

Figure 6.1. WCA data for the experimental coatings where the data points shown are means of three measurements and the error bars represent one standard deviation of the mean.

Results from characterization of the release properties via PB adhesion are shown in Figure 6.3. In these data, a trend similar to that seen in the WCA analysis was observed where the change in properties was slightly lessened for the pigmented coatings upon the inclusion of PDMS. The reduction in PB removal force caused by the inclusion of PDMS was not as substantial when 10% PDMS was included in the pigmented coatings. Therefore, a higher loading of PDMS was required to achieve the same reduction in PB adhesion compared to with the 0

PVC coatings. While an increased WCA and reduced PB adhesion were observed, a higher level of PDMS was necessary to achieve the same effect.

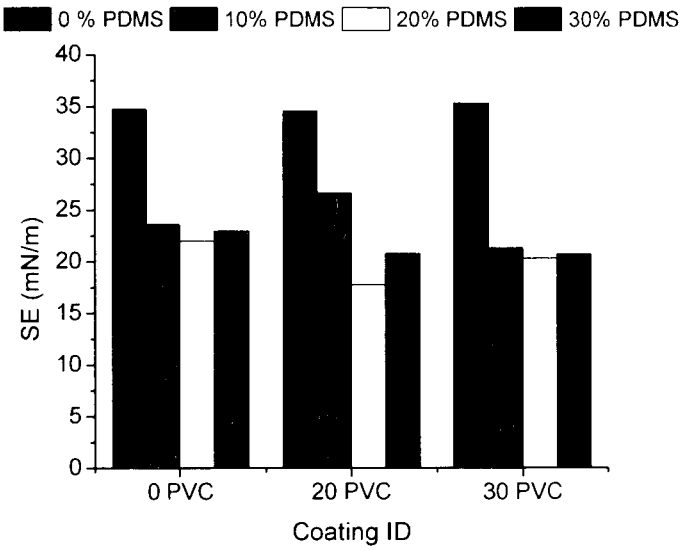

Figure 6.2. SE of cured films, as calculated from the Owens and Wendt method using the means of three WCA and MICA measurements.[21]

Figure 6.4 shows the 60° gloss for the pigmented coatings. As PDMS was added to the pigmented systems, a slight reduction in gloss was observed for the 20 PVC coatings and a more substantial drop was observed for the 30 PVC coatings when 30% PDMS was used. However, only the 30 PVC coating with 30% PDMS showed a significant reduction in gloss. This may have been caused by the inclusion of PDMS disrupting the dispersion quality when such high concentrations of both pigment and PDMS are used. It is important, however, that high gloss, pigmented coatings can be prepared where the inclusion of PDMS does not greatly affect the overall appearance and smoothness of the coatings.

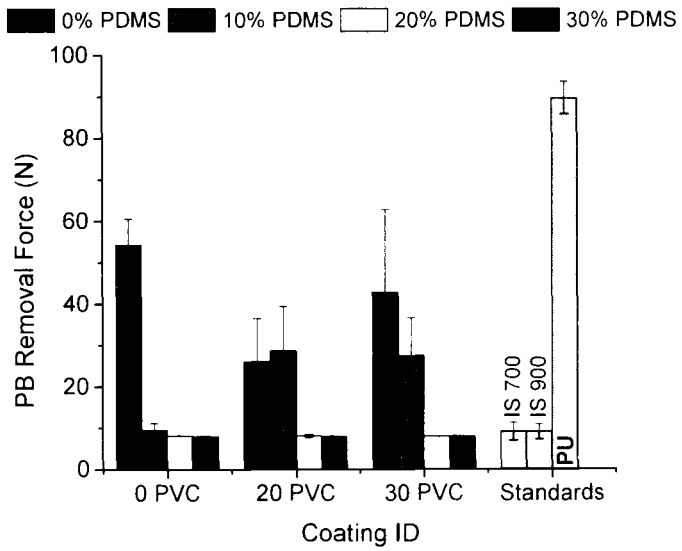

Figure 6.3. Pseudobarnacle adhesion of pigmented siloxane-polyurethane and standard coating systems where the reported values are means of at least six measurement attempts and the error bars represent one standard deviation of the mean.

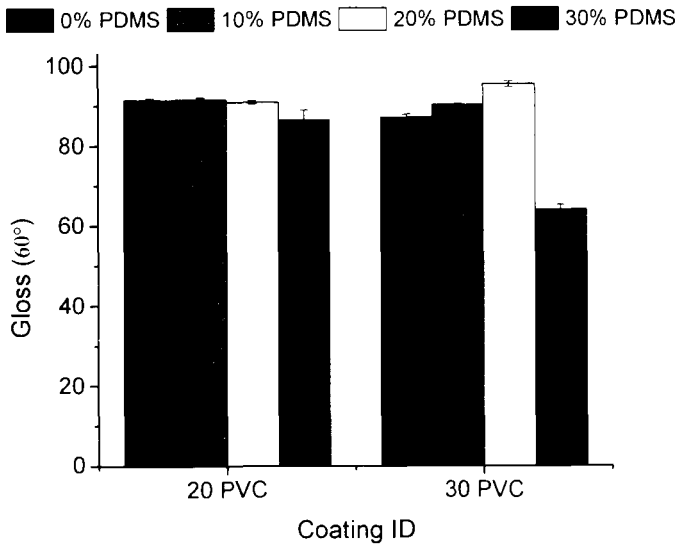

Figure 6.4. 60° gloss of pigmented coatings where the values are means of three measurements and the error bars represent one standard deviation of the mean.

Figure 6.5 shows the biofilm retention of *C. lytica* for the experimental and standard coatings. The values represent the amounts of bacteria that attached to the coating surface during incubation and are indicative of whether the coatings show antifouling performance. These coatings did not show antifouling behavior, as expected, since they do not contain active ingredients. It is shown in Figure 6.5 that the coatings exhibited similar *C. lytica* biofilm retention as silicone standard coatings, and slightly reduced biofilm retention compared to the polyurethane sample. Figure 6.6 shows the removal of *C. lytica* from the coating surfaces following water jetting at 20 psi for 5 sec. All of the coatings, with or without pigment and with or without PDMS showed similar removal, in the range of IS 700 and T2. IS 900 showed the highest removal of *C. lytica* biofilm, near 75% where the best of the experimental coatings showed approximately 65% removal. However, with similar removal values observed for all of the compositions, the effects of pigmentation seemed insignificant for the removal of *C. lytica*.

The attachment of *N. incerta* on the coatings is shown in Figure 6.7. Similar algal attachment was observed for all of the experimental and standard coatings. In some cases, there was a slight reduction in algal attachment as the PVC was increased, but most coatings exhibited comparable attachment. IS 900 showed the lowest attachment of diatoms, but this was only slightly reduced from the level of attachment observed on most other coatings. In Figure 6.8, the removal of *N. incerta* is shown with water jetting at 10 psi for 10 sec. The removal of diatoms was greater for coatings which included pigment, and greatest for those with 30 PVC. Additionally, the experimental coatings with higher PDMS loading showed greater

removal of *N. incerta* from the coating surface, especially at 30 PVC where almost 80% removal at 20 and 30% PDMS loading was observed. This removal was nearly double that observed for the commercial FR coatings, and slightly greater than the removal observed for the polyurethane standard. Typically, *N. incerta* adheres well to silicone based FR coatings and shows greater removal from the polyurethane standard than FR coatings. The high removal from the 30 PVC coatings suggests that pigmentation is contributing to the removal of *N. incerta* from these systems and could help improve performance for this type of coating, especially since even a slight slime layer can dramatically affect a ship's fuel efficiency[31].

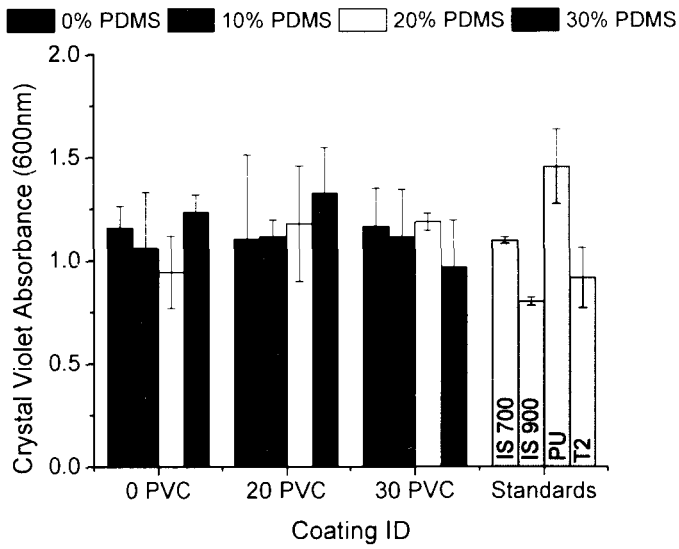

Figure 6.5. *C. lytica* biofilm retention on the experimental and standard coatings. The values shown are means of three measurements and the error bars represent one standard deviation of the mean.

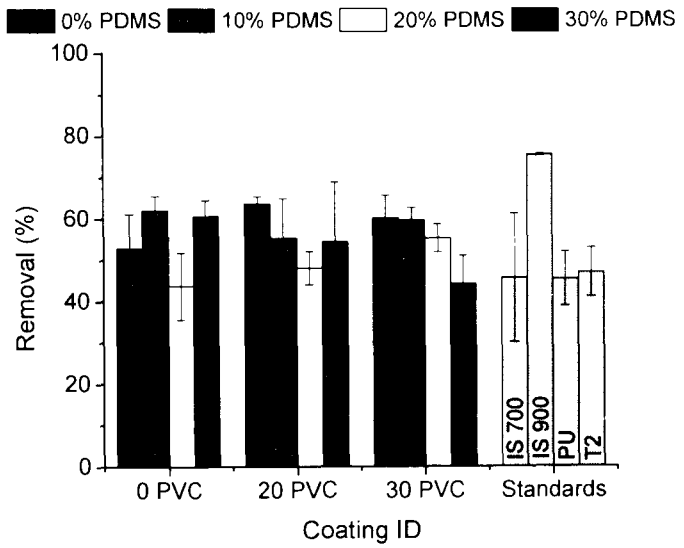

Figure 6.6. Removal of *C. lytica* after water jetting at 20 psi for 5 sec where the recorded values are means of three measurements and the error bars represent one standards deviation of the mean.

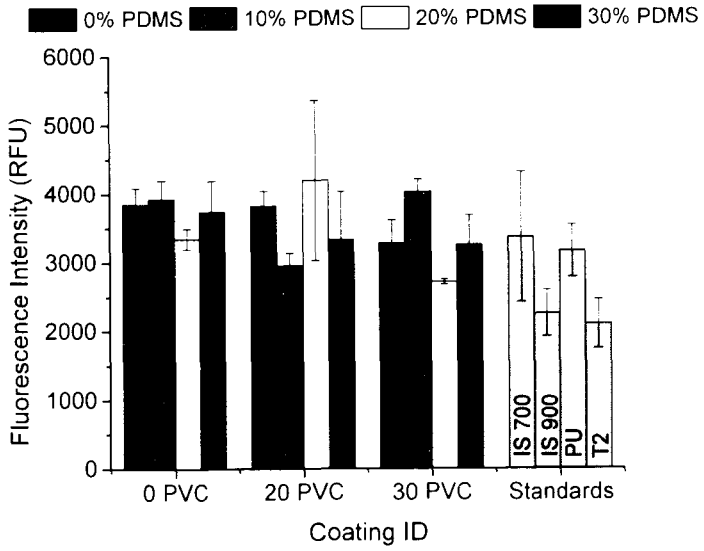

Figure 6.7. *N. incerta* algal attachment on the experimental and standard coatings where the data are means of three measurements and the error bars represent one standard deviation of the mean.

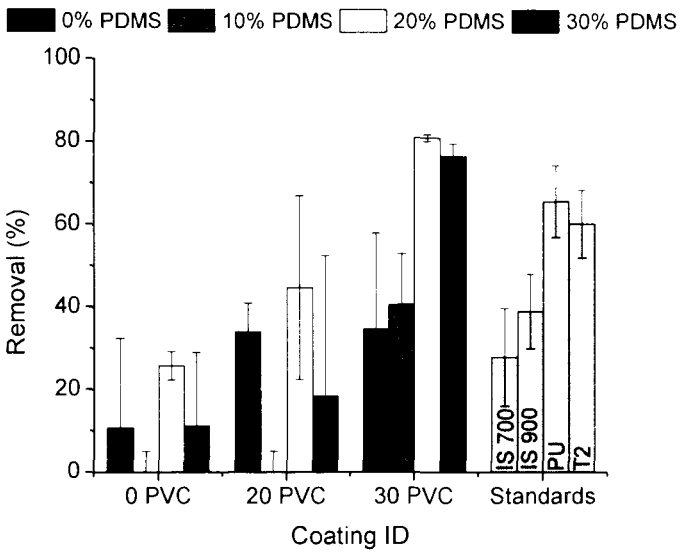

Figure 6.8. Removal of *N. incerta* after water jetting at 10 psi for 10 sec where the values represent the mean of three measurements and the error bars represent one standard deviation of the mean.

Results from the live adult barnacle reattachment assay are shown in Figure 6.9. Broken barnacles were observed on several occasions, where the removal force was too high and the barnacle broke before being dislodged from the coating surface. High removal forces and broken barnacles were observed for the coatings prepared without PDMS, at all levels of pigmentation. As the PDMS content was increased, fewer broken barnacles were observed and the average removal forces decreased. The coatings with each 10, 20, and 30% PDMS loadings all performed similarly in terms of barnacle removal force. This illustrates that there was little effect on barnacle adhesion by the pigmentation of these systems. While the performance was not greatly affected by the inclusion of pigment, the removal forces were higher than for commercial fouling-release coatings IS 700 and IS 900 from which all barnacles were removed and shell breakage was not an issue. On

the coatings that contained 30% PDMS, nearly all barnacles were removed without breaking, illustrating that these coatings can provide effective barnacle release, even if slightly higher forces are observed than for commercial FR coatings.

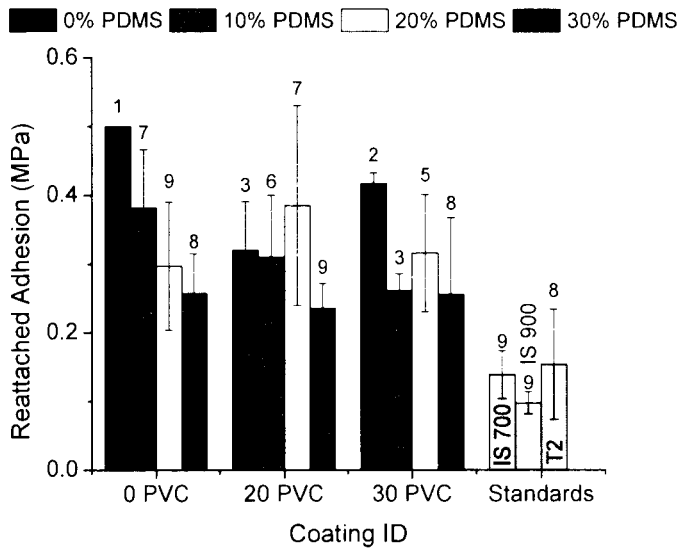

Figure 6.9. Removal forces of adult barnacles reattached to standard and experimental coatings. Nine measurements were attempted and broken barnacles were not included in this data. The data labels above each bar represent the number of measurements from which the data are composed. The value shown for each coating is the mean of the number of measurements shown. Error bars represent one standard deviation of the mean.

6.4. Summary and conclusions

Twelve siloxane-polyurethane coatings were prepared from pigment grinds of TiO_2 in an acrylic polyol, APT-PDMS and IDT. The coatings were prepared at 0, 20, and 30 PVC with PDMS loadings of 0, 10, 20, and 30%. WCA and SE characterization of the coatings showed that the PDMS had stratified to the surface of the coatings, due to increased in WCA and reduced SE compared to pure

polyurethane coatings without PDMS. A higher PDMS content was necessary to achieve the same increase in WCA for pigmented coatings when compared to those without pigment. A reduction in PB adhesion was observed when PDMS was included in the coating formulations. However, a PDMS loading of only 10% did not cause as dramatic reduction in PB removal force as when 20% or 30% loading was used in the pigmented systems. The pigmented coatings exhibited high gloss at both 20 and 30 PVC, but a reduction in gloss was observed at 30 PVC when the highest PDMS loading was used.

The FR performance of the coatings was not largely affected by the inclusion of pigment in the siloxane-polyurethane coatings. Removal of *C. lytica* from the coating surface was comparable to commercial FR systems and unpigmented systems performed similarly to pigmented experimental coatings. Removal of *N. incerta* increased with pigmentation, and high removal in some 30 PVC coatings was observed. Live barnacle reattachment showed similar barnacle removal for pigmented systems compared to unpigmented coatings. The removal forces of experimental coatings were higher than commercial FR standards, but inclusion of PDMS allowed for most barnacles to be removed without damaging or breaking their shells.

The properties and performance of the experimental coatings were generally consistent between pigmented and unpigmented coatings. This illustrates the potential of these systems to be formulated into paints for marine applications, as pigmentation did not dramatically affect their performance. The FR performance of all of the coatings was similar to commercial FR coatings in most cases. Slightly

increased barnacle adhesion was observed, but removal of microorganisms was comparable to the commercial coatings and most barnacles could be removed from the coatings when PDMS was included in the formulation. However, ocean site testing will need to be conducted to truly gauge the potential of these systems to perform as marine coatings. This publication represents screening experiments to assess the basic effect of pigmentation on these siloxane-polyurethane coatings where the addition of pigment has not adversely affected their performance. Ongoing work includes analysis of these systems at ocean sites where performance in a true marine environment and the effects of pigmentation is being further explored.

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CHAPTER 7. PIGMENTATION OF SILOXANE-POLYURETHANE FOULING-RELEASE COATINGS BASED ON PDMS MACROMERS

7.1. Introduction

Marine biofouling on sea-going vessels causes an increase in hydrodynamic drag which results in a number of undesirable issues.[1] The fuel consumption of a vessel may be increased by up to 40% and this causes an increase in emissions.[2] The maneuverability of a vessel is reduced, and the ship will not reach the same top operating speed as with a clean hull.[3] The detrimental effects on a ship's overall performance have led to the development of many coating systems for ship hulls to help prevent or minimize biofouling. Many of these coating systems have been based on toxic agents which prevent the fouling of vessels by releasing active ingredients which kill fouling or deter settlement. These are called antifouling (AF) coatings. Many effective AF paints have been developed, but some of the most effective active ingredients have been found to have negative effects on organisms that do not cause biofouling.[2] Therefore, recent focus has shifted toward the development of non-toxic coating systems such as fouling-release (FR) systems which function as release coatings and minimize the adhesion of biofouling organisms to a surface.[4]

Siloxane-polyurethane FR coatings have been developed at North Dakota State University as release coatings that offer durability and good biofouling release.[5] In these coatings, a reactive polydimethylsiloxane (PDMS) component is added to an aliphatic polyurethane coating system. Self-stratification occurs during film formation, where the PDMS component migrates to the coating surface due to

its low surface energy.[6] This process is dependent on the film formation process, solvent evaporation, vitrification, formulation viscosity, differences in surface energies, resin incompatibility, and the diffusion rate of the PDMS through the coating.[7,8] In clear coatings, self-stratified coatings have been fairly well studied, and found that two coatings layers can be prepared from a single formulation, if specific parameters are met. However, pigmented self-stratified coatings have been less studied, and pigmentation is known to affect the diffusion of additives to the surface of coatings.[9] The diffusion rate of PDMS through the coating may be reduced, as the molecules have to migrate around pigment particles to reach the surface, and this must happen before being reacted into the polymer network. Pigmentation is important parameter to explore for marine coatings, as commercial coatings often require the use of pigment for coloration, and/or to see where a coating has been applied or is wearing away.

In this work, the effects of pigmentation in siloxane-polyurethane FR coatings prepared with PDMS macromers were explored. Different from Chapter 7, this chapter discusses coatings prepared with PDMS macromers with monofunctionality, rather than difunctional PDMS. General coating properties and FR performance of twenty-eight unique coating formulations are discussed, where titanium dioxide (TiO_2) was used as a model pigment. The effect of pigmentation (0, 10, 20, and 30 PVC), PDMS binder loading (0%, 10%, 20%, and 30% mass), and pigment dispersing aid (Dipserbyk-2150 and Disperbyk-161) on coating water contact angle, surface energy, hiding capabilities, gloss, and solvent resistance were explored. Additionally, high throughput FR laboratory bioassays were used to

rapidly evaluate the FR performance of these coatings. The preparation of the coatings, and their properties and R performance are discussed.

7.2. Experimental

7.2.1. Materials

Organically treated titanium dioxide (TiO_2) R-706 pigment and Vazo® 67 (2,2'-Azobis(2-methylbutyronitrile)) were generously supplied by DuPont. Inhibitor free tetrahydrofuran (THF), lithium trimethylsilanolate (LTMS, 1.0 M in dichloromethane), methylene iodide, acetyl acetone (2,4-Pentanedione, PD), butyl acrylate, hydroxyethyl acrylate, and dibutyltin diacetate (DBTDAc) were purchased from Sigma-Aldrich. Desmodur Z4470 BA (Isophorone diisocyanate trimer (IDT), 70% in butyl acetate) was generously provided by Bayer MaterialScience. Toluene and tetrahydrofuran were purchased from VWR International. Methyl amyl ketone was supplied by Eastman Chemical. Hexamethylcyclotrisiloxane (D_3) and dimethylchlorosilane (DMCS) were purchased from Gelest, Inc. The pigment dispersing aids Disperbyk-2150 and Disperbyk-161 were generously supplied by Byk-Chemie. All materials were used as received, without further purification.

Standard coating systems were prepared for comparison in laboratory fouling-release bioassays. Intersleek® 700 (IS 700) and Intersleek® 900 (IS 900) were received from International Paint and prepared according to manufacturer's specifications. Silastic® T2 (T2) was received from Dow Corning, prepared according to their specifications and thinned with methyl isobutyl ketone. A polyurethane control coating (PU) was prepared from IDT and a polycaprolactone triol (Capa® 3050) supplied generously by Perstorp.

Dr. Michael Hadfield of the Kewalo Marine Laboratory, University of Hawaii generously provided the marine bacterium *C. lytica*. The marine diatom *N. incerta* was provided by Dr. Maureen Callow of the University of Birmingham, UK. Artificial seawater (ASW) was prepared by dissolving 38.5g of sea salts (Sigma-Aldrich) into 1L of deionized water. Bacterial biofilm growth medium (BGM) consisted of 0.1g yeast extract and 0.5g of peptone per 1L of ASW. Algal growth medium (F/2) consisted of 1L of ASW supplemented with nutrients to generate Guillard's F/2 medium.[10] BGM, F/2 and ASW were filter sterilized with 0.2 micron vacuum-cap filters. Crystal violet powder, 33% glacial acetic acid and dimethyl sulfoxide (DMSO) were purchased from VWR International and used as received.

7.2.2. Preparation and characterization of acrylic polyol

An acrylic polymer with hydroxyl functionality was prepared using a starved-feed polymerization method in toluene, as has been described in previous chapters. A 5000 ml four-neck reaction apparatus was charged with toluene (960 g) and heated to 80°C. The addition of a monomer mixture (BA: 1200 g, HEA: 300 g, Vazo 67: 60 g, toluene: 540g) was carried out over three hours with a feed rate of 12-13 mL min^{-1}. The temperature was maintained at 90-100°C during addition and at 95°C for 30 minutes afterward. A chaser solution of Vazo 67 (6 g) and toluene (54 g) was added and the temperature was maintained for one hour. The mixture was cooled to room temperature with mechanical stirring.

7.2.3. Preparation of pigment grinds in acrylic polyol

Pigment grinds of TiO_2 were prepared in the acrylic polyol. The acrylic polyol and pigment dispersing aid were measured into a steel beaker and stirred to

mix, using a high speed disperser affixed with a Cowles blade. The pigment dispersants Disperbyk-2150 and Disperbyk-161 were added so that their concentrations were 4% and 5.5% weight based on the TiO_2. Pigment dispersion was carried out using high speed so that an appropriate "doughnut" conformation was achieved in the metal beaker.[11] The liquid was drawn downward in the center of the beaker by the dispersing blade, and pushed upward on the outside of the beaker. Toluene was added as a solvent to reduce the pigment grind viscosity as needed. The pigment grinds used in the formulation of siloxane-polyurethane coatings are summarized in Table 7.1. Fineness of dispersion and Hegman values were determined in accordance with ASTM D1210.

Table 7.1. Pigment grinds prepared for the formulation of pigmented siloxane-polyurethane coatings.

				Dispersing Aid		
Grind #	Polyol (g)	Toluene (g)	TiO_2 (g)	Name	Mass (g)	Hegman Value
1	257.2	80.0	681.3	Disperbyk-2150	27.2	6
2	257.5	142.2	683.9	Disperbyk-161	37.5	6-7

7.2.4. PDMS macromer polymerization

The preparation of 30,000 g/mol APT-PDMS-M was conducted in a similar manner and has been described in previous chapters. A 50% weight solution of D_3 (305 g) was added to a nitrogen (N_2) purged 500 ml RBF. The solution was degassed by bubbling N_2 through it for 1 hr in a sealed flask in the presence of molecular sieves. The polymerization of D_3 was initiated by the addition of LTMS solution (4.8 g) to the sealed flask, and was allowed to proceed at room temperature for 3 hr. DMCS (3.5 ml) was added to terminate the polymerization.

7.2.5. PDMS macromer functionalization

The hydrosilylation of HT-PDMS-M and allylamine was performed to yield monoamine terminated PDMS macromer (APT-PDMS-M). Allylamine (4.8 g) and chloroplatinic acid hexahydrate (0.06 g) were dissolved in inhibitor-free THF (6.4 g) in a 100 ml RBF that was purged with N_2 and sealed. The mixture was degassed for 15 min with magnetic stirring and then heated at 60°C for 1 hr. The solution was added to a N_2 purged 500 ml RBF with HT-PDMS-M (94 g). The reaction mixture was heated at 90°C for 24 hr with magnetic stirring.

7.2.6. Characterization of PDMS macromer and acrylic polyol

7.2.6.1. Rapid® GPC: High-throughput gel permeation chromatography (GPC) was used to confirm the molecular weight of the PDMS macromer, relative to polystyrene standards. The polymer solution was prepared at a 2 mg mL^{-1} in stabilized THF. Analysis was performed using a Symyx® Rapid GPC with an evaporative light scattering detector (PL-ELS 1000), 2xPLgel Mixed-B columns (10 µm particle size) and a flow rate of 2.0 mL min^{-1}.

7.2.6.2. Percent solids and conversion of acrylic polyol: The final concentration of the polyol was 50% by mass in toluene. The resulting polymer was characterized for percent solids and percent conversion in accordance with ASTM D2369.

7.2.7. Pigmented siloxane-polyurethane coating formulation

The formulation of pigmented siloxane-polyurethane coatings was carried out by mixing the following ingredients together: APT-PDMS-M, Desmodur Z 4470 BA (IDT), pigment grind (acrylic polyol and TiO_2), additional acrylic polyol, PD, and

DBTDAc catalyst solution. First, the APT-PDMS-M and IDT were added to formulation cups and mixed together overnight via magnetic stirring at room temperature. The following morning, the DBTDAc catalyst solution was added and the formulations were shaken to mix and magnetically stirred. The PD pot-life extender was added, followed by the pigment grinds and additional acrylic polyol. A single pigment grind was used in the preparation of all the coatings with each dispersing aid. Therefore, acrylic polyol (additional to that in the pigment grinds) was added to achieve the appropriate formulation parameters (i.e. PVC, ratio of functional groups, etc.) The paint formulations were stirred using wooden paint sticks until a homogeneous formulation was obtained, and then magnetically stirred for 60-90 min prior to coating application. Table 7.2 outlines the amounts of materials used to formulate each pigmented coating formulation. Table 7.3 details the solid composition of each coating, based on solid mass percentage.

7.2.8. Pigmented siloxane-polyurethane coating preparation and curing

Siloxane-polyurethane coatings were prepared on different substrates, depending on their use. Coatings used in laboratory biological assays to assess fouling-release performance were prepared by deposition in microtiter plates onto aluminum disks primed with Intergard 264 (70-80 μm). The coating formulations were deposited into the wells using volumetric repeat pipets (250 μl per well). Gentle agitation was used to ensure that the entire primed surface was covered with coating formulation. Coatings used in coating property testing were applied on primed and bare aluminum panels (4 x 8 in. and 3 x 6 in., 0.6 mm thick, type A, alloy 3003 H14, obtained from Q-lab) and glass panels. Coatings were applied to

Table 7.3. Mass percent solid coating composition of siloxane-polyurethane coatings based on PDMS macromers.

			Soids Mass %			
PVC	PDMS	Dispersing Aid	TiO2	Acrylic Polyol	IDT	PDMS
0	0%	None	0.00%	60.06%	39.94%	0.00%
0	10%	None	0.00%	53.75%	36.12%	10.14%
0	20%	None	0.00%	47.78%	32.23%	19.98%
0	30%	None	0.00%	41.79%	28.67%	29.53%
10	0%	Disperbyk-2150	26.99%	43.56%	29.45%	0.00%
10	10%	Disperbyk-2150	27.35%	38.69%	26.30%	7.67%
10	20%	Disperbyk-2150	27.68%	34.23%	23.35%	14.74%
10	30%	Disperbyk-2150	28.04%	29.92%	20.58%	21.47%
20	0%	Disperbyk-2150	45.62%	32.23%	22.15%	0.00%
20	10%	Disperbyk-2150	46.05%	28.57%	19.79%	5.59%
20	20%	Disperbyk-2150	46.39%	24.96%	17.49%	11.17%
20	30%	Disperbyk-2150	46.88%	21.48%	15.20%	16.44%
30	0%	Disperbyk-2150	59.19%	24.03%	16.78%	0.00%
30	10%	Disperbyk-2150	59.66%	21.15%	14.96%	4.23%
30	20%	Disperbyk-2150	60.13%	18.41%	13.23%	8.23%
30	30%	Disperbyk-2150	60.53%	15.74%	11.50%	12.23%
10	0%	Disperbyk-161	24.85%	44.49%	30.66%	0.00%
10	10%	Disperbyk-161	25.19%	39.45%	27.38%	7.98%
10	20%	Disperbyk-161	25.45%	35.06%	24.54%	14.95%
10	30%	Disperbyk-161	25.82%	30.28%	21.40%	22.50%
20	0%	Disperbyk-161	43.16%	33.16%	23.68%	0.00%
20	10%	Disperbyk-161	43.66%	29.32%	21.22%	5.80%
20	20%	Disperbyk-161	44.19%	25.29%	18.64%	11.88%
20	30%	Disperbyk-161	44.57%	21.71%	16.37%	17.35%
30	0%	Disperbyk-161	57.38%	24.37%	18.25%	0.00%
30	10%	Disperbyk-161	57.85%	21.27%	16.38%	4.50%
30	20%	Disperbyk-161	58.30%	18.26%	14.39%	9.05%
30	30%	Disperbyk-161	58.73%	15.35%	12.53%	13.39%

7.2.9. Characterization of pigmented siloxane-polyurethane coatings

7.2.9.1. Contact angle and surface energy analysis: Contact angle and surface energy analysis was performed on coatings prepared by drawdown on unprimed aluminum panels using a Symyx®/First Ten Ångstroms™ Coating Surface Energy System. Three droplets of each water and methylene iodide were

measured in contact angle analysis. The mean values from contact angle measurement with these liquids were used in the calculation of surface energy using the Owens-Wendt method.[12]

Contact angle analysis was also performed on coatings that were removed from glass panels. These coated panels were immersed in water for approximately 2 hr after which they were easily removed from the glass substrate to yield free films. After drying for 24 hr under ambient conditions, the free films were used for contact analysis where water contact angle was measured at each the coating/air interface (top) and the former coating/glass substrate interface (bottom). Three water droplets were measured in each case.

7.2.9.2. Contrast ratio: Contrast ratio measurements were performed using coating free films (removed from glass panels). The films were placed over Leneta charts for measurement of coating reflectance (Y-tristimulus value) over each of the black and white regions of the chart, using a MacBeth Color Eye (ASTM D2805). The ratio of the reflectance values obtained were used in the calculation of the contrast ratio of the films using the equation below (7.1) where C_w is the contrast ratio, R_0 is the reflectance of the film over the black portion of the Leneta chart, and R_w is the reflectance of the film over the white portion of the Leneta chart.

$$C_w = \frac{R_0}{R_w} \tag{7.1}$$

7.2.9.3. Gloss: Gloss measurements (60°) were obtained using a Byk-Gardner micro-TRI-gloss gloss meter (ASTM D523). Coatings prepared on bare aluminum panels were used in this analysis and three measurements were taken

on each coating. The mean and standard deviation of these measurements were recorded.

7.2.9.4. MEK (methyl ethyl ketone) double rubs: A single coating on an unprimed aluminum panel was used in the analysis of solvent resistance by MEK double rubs (ASTM D5402). A hammer head was wrapped with four layers of cheesecloth which was fixed with thin wire. The cheesecloth was saturated with MEK and the hammer head was rubbed across the coating. The cheesecloth was dipped in solvent after every five double rubs. At this time, the coating sample was also checked for failure in the form of coating marring, blistering, of wearing through to the substrate. The cheesecloth was replaced after failure was observed.

7.2.9.5. Pseudobarnacle adhesion: Pseudobarnacle (PB) adhesion measurements were made using an Symyx® Automated Pull-off Adhesion System where the adhesion of an epoxy-glued aluminum stud to the coating surface was measured.[13] The coated panels were placed onto vacuum plates which held them in place for the application of epoxy into designated regions. A plastic template with 24 patches of 7 mm diameter holes was placed over the panels. The two-component epoxy adhesive (Loctite® Hysol® 1C-LV) was mixed and spread over the plastic template using a putty knife. The spreading of the epoxy over the template deposited adhesive through the 7 mm holes of the template, onto the coatings. The panels were placed into clamping jigs with holes which aligned with the plastic template. Pseudobarnacles were placed in the holes of the clamping jig, atop the epoxy adhesive that was deposited onto the coatings. Six PB were applied to each coating, and weighted foam blocks were placed atop the PB

adhesion apparatus to ensure uniform adhesion of the PB to the coatings. The adhesive was allowed to cure overnight. The following day, the weighted foam blocks were removed and the panels (enclosed in clamping jigs) were placed in the automated adhesion system. The PB were removed by an automated pull-off head which applied gradual force, individually to each PB until it was removed from the surface. The force at release was recorded for each PB, and the mean and standard deviation were calculated.

7.2.10. Assessment of pigmented siloxane-polyurethane fouling-release performance via laboratory bioassays

7.2.10.1. Coating pre-leaching and leachate toxicity analysis: The coatings used in the fouling-release biological assays were pre-leached prior to analysis to ensure that any toxic agents which may have been present in the coatings were removed prior to analysis.[14] Pre-leaching was carried out by placing the coated panels on racks and immersing them in recirculating, clean deionized water tanks where the water was changed daily. Pre-leaching was carried out for four weeks prior to analysis of leachate toxicity. In 24-well microtiter plates where the coatings had been deposited, ASW and nutrients were added. The growth of marine bacteria and microalgae were monitored in the extraction liquid over 24 hr. The growth of the bacteria was quantified by staining with crystal violet and quantifying with absorbance measurements at 600 nm. The growth of the microalgae was monitored by measuring the fluorescence of chlorophyll (excitation wavelength: 360 nm, emission wavelength: 670 nm). Negative leachate toxicity was confirmed by comparison of bacterial and microalgal growth with negative growth controls.

7.2.10.2. Bacterial biofilm retention and removal: High-throughput assessment of bacterial (*C. lytica* and H. *pacifica*) biofilm retention on coatings prepared in 24 well microtiter plates has been previously described.[14-16] The plate wells were inoculated with 1.0 ml of bacteria (*C. lytica*: 10^7 cells ml^{-1} in BGM, H. pacifica: 10^8 cells ml^{-1} in ASW). Incubation was carried out at 28°C for 24 hr. The BGM and suspended bacteria were discarded, and the retained biofilm was rinsed three times with ASW to remove unattached or weakly attached biofilm. The retained biofilms were stained with crystal violet (0.3% w/v in deionized water) after being dried under ambient conditions for 1 hr. The crystal violet stain was extracted with glacial acetic acid (0.5 ml, 33%) and quantified by absorbance measurements at 600 nm. Three replicates were measured for each coating, and the absorbance measurements were considered directly proportional to the retained biofilm on the coating surfaces.

The removal of bacteria from the coating surfaces was analyzed by water jetting with a rotating water jet and quantification by extraction of crystal violet.[17] The wells of microtiter plates were inoculated incubated as described above. Following incubation, the retained biofilms were rinsed three times to remove weakly or unattached biofilms, and the biofilms were dried under ambient conditions for 1 hr. Three replicate wells were left untreated to account for initial bacterial attachment, and three were water jetted with the rotating water jet at 20 psi (*C. lytica*) or 25 psi (*H. pacifica*) 5 sec. Remaining biofilm was stained with crystal violet and quantified as described above. The removal of bacteria was

calculated as the difference between wells treated and untreated with the rotating water jet.

7.2.10.3. N. incerta *attachment and removal:* The quantification of *N. incerta* attachment and removal has been previously described.[18-20] Coatings prepared in 24 well microtiter plates were inoculated with 1.0 ml of *N. incerta* suspension (10^5 cells ml^{-1}) in F/2. Incubation was carried out for 2 hr under ambient conditions. Water jetting of the attached biofilm (20 psi, 10 sec) was carried out on four replicate wells of each coating. Four replicate wells for each coatings were left untreated to account for the initial algal attachment. Following water jetting, the biofilm (initial attachment, or remaining biofilm after water jetting) was incubated in ambient darkness for 30 min in DMSO (0.5 ml). Gentle agitation was used to yield a homogeneous sample, and 0.2 ml of this sample was transferred to a 96 well plate for fluorescence measurements and the quantification of chlorophyll (excitation wavelength: 360 nm, emission wavelength: 670 nm). The percent of algal removal was calculated as the difference in relative fluorescence units (RFU) for untreated wells and those which were water jetted.

7.2.10.4. Barnacle reattachment: An adult barnacle reattachment assay was used to assess the fouling-release performance of the coatings with respect to shell fouling. Nine adult barnacles (*Amphibalanus amphitrite*) with a basal diameter of approximately 5 mm were removed from a silicone substrate and placed on the coating panels. The barnacles were allowed to reattach to the coating surfaces during immersion in an ASW aquarium system for 14 days with daily feedings of brine shrimp nauplii. The reattached barnacles were dislodged from the coating

surfaces using a hand held digital force gauge (ASTM D5618). A digital force gauge was placed at the barnacle base plate, parallel to the coating surface, and pushed laterally (in shear) until it became detached from the surface. Once detached, the areas of the barnacle base plates were measured using image analysis (Sigma Scan Pro5.0). Barnacle adhesion strengths were calculated from the removal forces and surface areas of the barnacle base plates. The adhesion values for each coating were reported as the mean of the total number of barnacles exhibiting a measurable removal force. During testing of well adhered barnacles, the organism's shell sometimes broke before the barnacle became dislodged from the coating. In these cases, the removal force was not included in the calculation of the mean, and the number of broken barnacles was recorded as part of the measurement.

7.3. Results and discussion

The results from the GPC characterization of the polymers used in the preparation of siloxane-polyurethane FR coatings are shown in Table 7.4. The table shows that the molecular weight of the PDMS macromer was close to that targeted for the polymerization, and the polydispersity of the macromer was low. Together, these indicate the effectiveness of the anionic polymerization where the molecular weight was controlled by the ratio of initiator to monomer, and the polydispersity was close to unity. The monomer conversion in the polymerization of the acrylic polyol was high. Together with the hydroxyl equivalent weight, this suggests that individual polymer chains had multiple hydroxyl groups to establish a crosslinked network within the coating system.

Table 7.4. GPC results from characterization of PDMS macromer and acrylic polyol used in the preparation of siloxane-polyurethane coatings.

Polymer	Target MW (g mol^{-1})	$\overline{M_n}$	$\overline{M_w}$	PDI	Conversion	Equivalent Weight (g $equiv^{-1}$)
PDMS	30,000	23,500	29,900	1.27	NM	30,000 (NH_2)
Acrylic	NA	9,300	14,400	1.55	99%	580 (OH)

NA: Not applicable, NM: Not measured

Twenty-eight unique siloxane-polyurethane coatings were prepared based on PDMS macromers where the PVC, PDMS binder content, and pigment dispersing aid were varied. Four coatings were prepared without pigment, where the PDMS binder content was varied at 0, 10, 20, and 30% based on mass. Twelve coatings were prepared with each pigment dispersing aid Disperbyk-2150 and Disperbyk-161 where the PVC was varied at 10, 20, and 30 PVC and the PDMS binder content was varied at 0, 10, 20, and 30% based on mass. The maximum PVC (30) was selected, as it was approximately half of the theoretical critical PVC (CPVC) for the TiO_2 pigment used in the study, as calculated from oil adsorption values for the specific TiO_2 used.

The water contact angles (WCA) of the coatings examined in this study are shown in Figure 7.1. The surface energies of the coatings, as calculated from the Owens-Wendt method using mean water and methylene iodide contact angles are displayed in Figure 7.2. WCA obtained on free films where the hydrophobicity of the former coating/air interface and coating/substrate interface were studied are shown in Figures 7.3 and 7.4. As shown in Figure 7.1, the WCA of the coatings containing PDMS were higher than those on coatings prepared without PDMS. The WCA of the PDMS containing coatings was greater than 100° in nearly every

case, whereas coatings without PDMS showed much lower WCA near 80°. Coatings without pigment showed higher WCA than those prepared with pigment at 10% and 20% PDMS binder loading. However, when 30% PDMS was incorporated, the coatings with and without pigment showed similar WCA, but the WCA was slightly lowered as the PVC was increased. Overall, the pigment dispersing aid did not affect the WCA of the pigmented films.

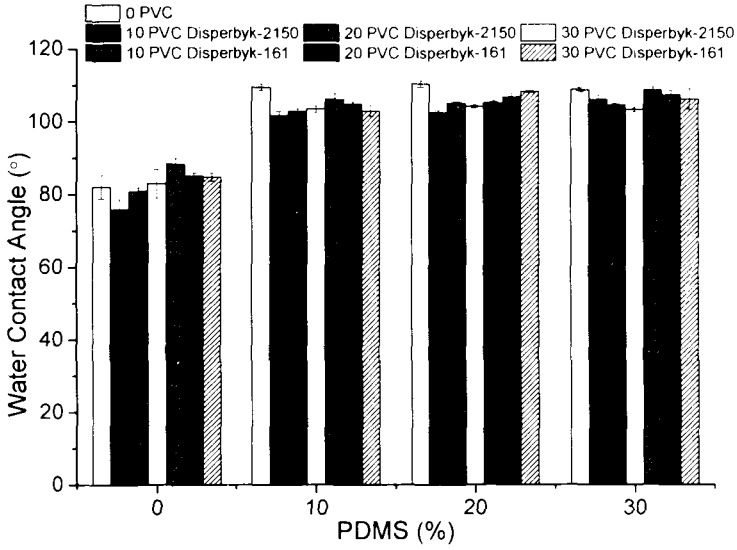

Figure 7.1. Water contact angle (WCA) of pigmented siloxane-polyurethane coatings prepared with PDMS macromers. The measurements shown are the means of three measurements and the error bars represent one standard deviation of the mean.

The surface energies (SE) of the coatings (Figure 7.2) were lower for coatings prepared with PDMS than for those prepared without PDMS. The coatings prepared without pigment showed similar SE at all PDMS loadings, approximately 25 mN/m. The pigmented coatings showed some variation in SE, ranging from 20-35 mN/m, but the pigment dispersing aid did not seem to affect the SE of the coatings. However, most of the coatings had SE in the range of 20-

25 mN/m, which is similar to that observed for coatings that did not contain pigment. The slightly lower WCA and slightly increased SE for the pigmented coatings illustrates that pigmentation may have had a slight effect on the self-stratification of these coatings during which PDMS migrated to the coating surface. However, because the WCA were still high and SE were still low, the effect was minimal and the trend did not propagate as higher levels of pigment were added. This indicates that only a slight effect was caused by pigmentation, as the coatings with 30 PVC did not show dramatically different results than those with 10 PVC.

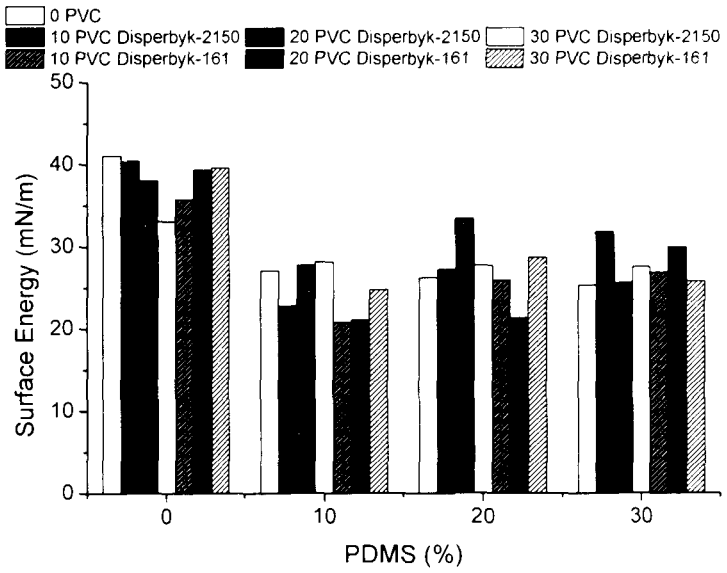

Figure 7.2. Surface energy of pigmented siloxane-polyurethane coatings prepared with PDMS macromers. The surface energies were calculated from the mean values of three water and methylene iodide contact angles using the Owens-Wendt method.[12]

Figures 7.3 and 7.4 summarize WCA analysis that was performed on the top surfaces (original coating/air interface) and bottom surfaces (original coating/substrate interface) of pigmented siloxane-polyurethane free films that

were removed from glass substrates. As shown, there was a difference in WCA on the top and bottom surfaces of the free films in every case. The WCA was always higher on the top surfaces of the free films, even for coatings which did not contain PDMS. This suggests that there were differences in the two interfaces that were not dependent on the presence of PDMS. This may have been caused by surface roughness at the coating/air interface, or the migration of other materials within the film (i.e. pigment dispersing aid, contaminant).

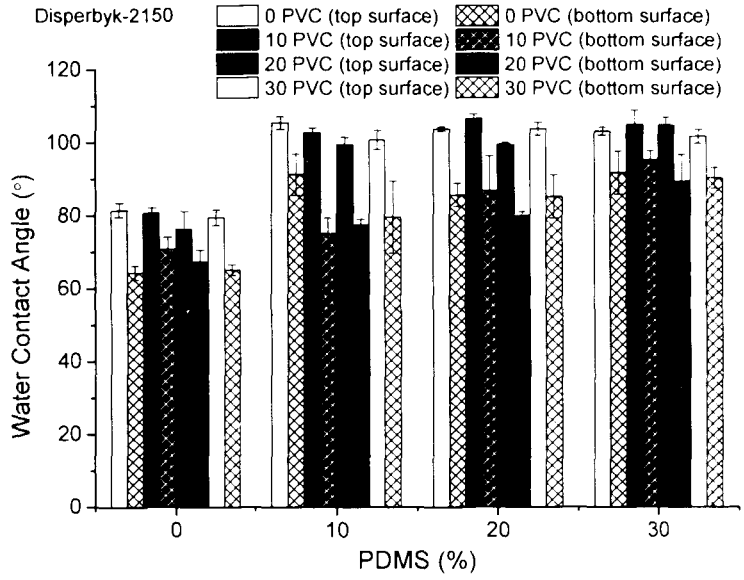

Figure 7.3. Water contact angle of free films of siloxane-polyurethane coatings prepared with Disperbyk-2150. The "top surface" of the coating was coating/air interface and the "bottom surface" of the coating was the coating/substrate interface. The values are the means of three measurements and the error bars represent one standard deviation of the mean.

In this analysis, it was also shown that larger differences in WCA were observed for coatings prepared with PDMS, in some cases. For instance, the coatings prepared with 10% PDMS binder loading showed the largest difference in

WCA when comparing the top and bottom surfaces of the films and this was true for both dispersing aids and at 10 and 20 PVC. The coatings prepared at 30 PVC with Disperbyk-161 showed large differences in the WCA from the top to bottom surfaces of the films whereas those prepared with Disperbyk-2150 showed smaller differences for those coatings prepared at 30 PVC. Overall, the data in Figures 7.3 and 7.4 help to illustrate that PDMS is segregating to the coating surface during film formation, as the WCA for the tops of the films was higher than the bottoms. Pigmented coatings and coatings containing PDMS showed greater differences between the WCA from the tops of the coatings and WCA from the bottoms of the coatings. Self-stratification has occurred in the films, and other factors such as pigment dispersing aid, surface roughness, or arrangement or atoms at the interfaces is also affecting the measured WCA shown here.

The pseudobarnacle adhesion obtained for the twenty-eight coatings is shown in Figure 7.5. The coatings prepared with pigment showed higher PB removal forces than coatings which did not contain TiO_2. This indicates that the addition of pigment affected the PB release. As indicated with the subtle changes in WCA and SE, pigmentation seemed to slightly affect the self-stratification of the siloxane-polyurethane coatings, resulting in a less hydrophobic surface to which PB adhesion was higher. Coatings prepared with the pigment dispersing aid Disperbyk-161 showed higher PB adhesion at 20% PDMS binder loading. However, at 30% PDMS binder loading, all of the coatings showed very low, similar PB adhesion, illustrating that formulation of siloxane-polyurethane coatings

with low PB adhesion can be obtained if higher levels of PDMS are used in the binder.

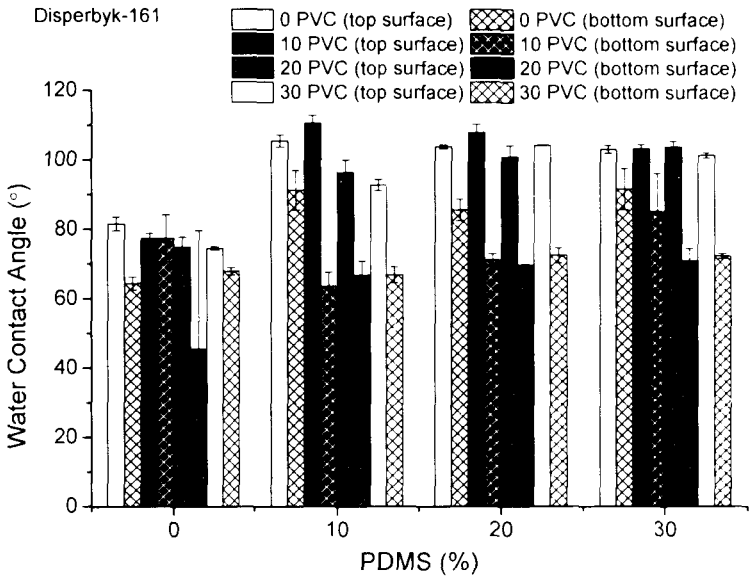

Figure 7.4. Water contact angle of free films of siloxane-polyurethane coatings prepared with Disperbyk-161. The "top" of the coating was coating/air interface and the "bottom" of the coating was the coating/substrate interface. The values are the means of three measurements and the error bars represent one standard deviation of the mean.

The contrast ratios of the pigmented siloxane-polyurethane coatings were measured to determine the ability of the coatings to hide a colored substrate. The results from this analysis are shown in Figure 7.6 where high values (near one) are indicative of the ability of the paints to hide a substrate. The contrast ratios increased as the PVC of the coatings increased. The inclusion of more pigment allows for scattering of more light that enters a coating. However, the coatings exhibited high contrast ratios at even 10 PVC, and the samples were only approximately 80 μm in thickness. Therefore, these data illustrate that satisfactory

not largely impact the gloss of the systems. In general, moderate to high levels of gloss were obtained for the coatings.

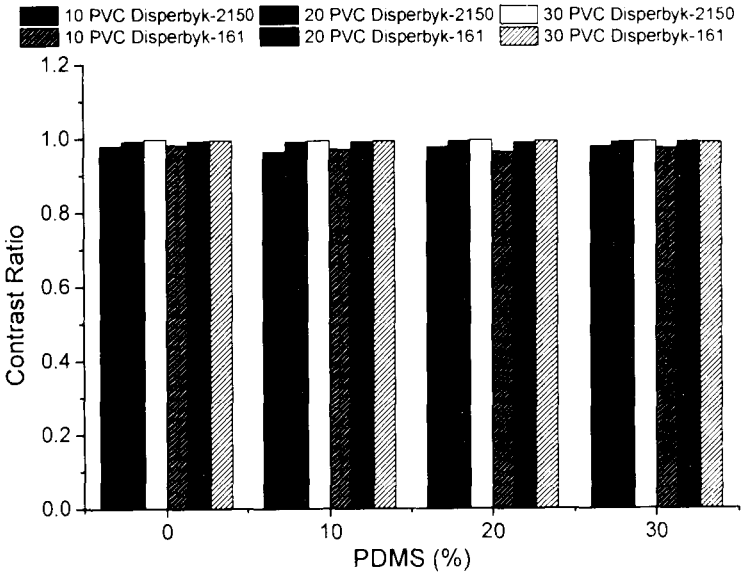

Figure 7.6. Contrast ratio of pigmented siloxane-polyurethane coatings based on PDMS macromers.

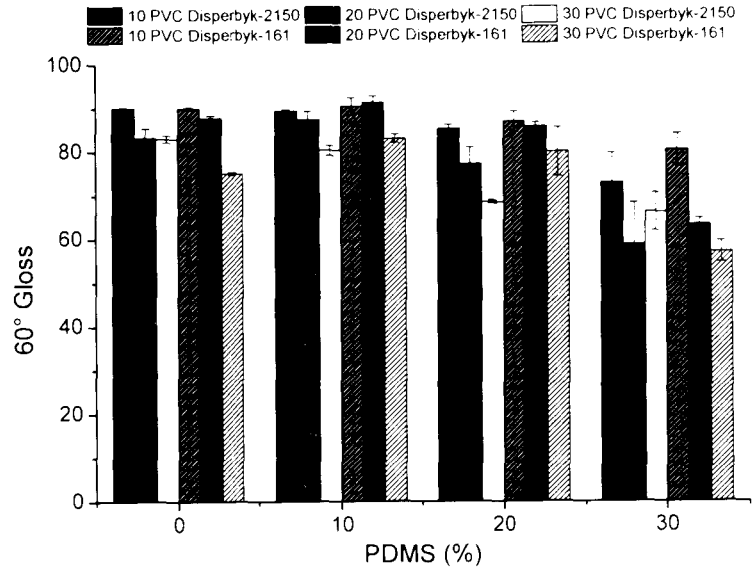

Figure 7.7. Gloss (60°) of pigmented siloxane-polyurethane coatings based on PDMS macromers. The values represent the means of three measurements and the error bars represent one standard deviation of the mean.

MEK double rub data for the siloxane-polyurethane coatings based on PDMS macromers are shown in Figures 7.8 and 7.9. The data show reduced solvent resistance with increased PDMS binder content. This may be due to a reduction in crosslink density by the inclusion of PDMS, where the amine groups on PDMS macromers react with isocyanate groups in the polyurethane coating and prevent the reacted isocyanate groups from forming bonds with hydroxyl groups on the polyol which would contribute to the crosslinking of the coating. Even though the ratio of isocyanate groups to amine and hydroxyl groups was kept constant for all of the coatings, increasing the number of amine groups effectively decreased the number of hydroxyl groups with which the isocyanate could react. The addition of PDMS in the coatings may have also added to effective free volume in the coatings if there were PDMS domains distributed within the polyurethane, even if they were concentrated toward the coating surface. Increased PVC increased the solvent resistance of the coatings. The inclusion of pigment could have effectively lengthened the diffusion pathway for solvent to enter the coating, causing an increase in solvent resistance. The pigment dispersing aid did not show a clear influence on solvent resistance, as some coatings prepared with Dipserbky-2150 showed greater solvent resistance than comparable coatings prepared with Disperbyk-161, and the reverse was true for some compositions also. PDMS binder content and PVC had greater impacts on solvent resistance and variation dependent on dispersing aid may have been due to testing variability, as only one measurement was made per coating.

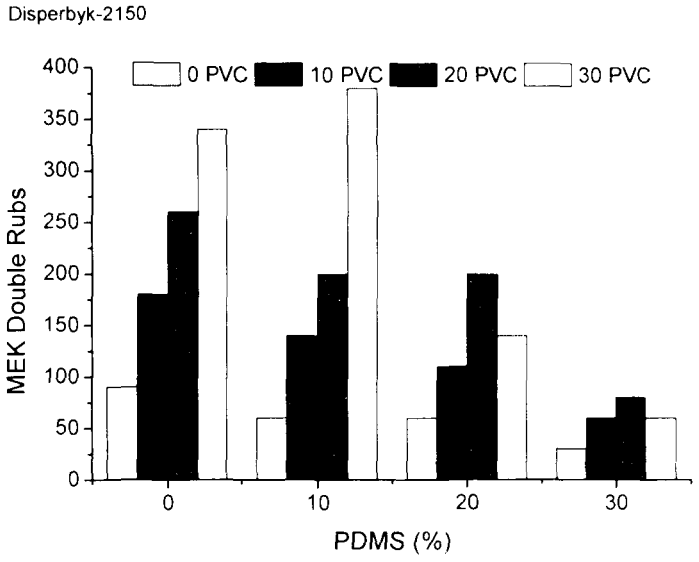

Figure 7.8. MEK Double rubs of siloxane-polyurethane coatings based on PDMS macromers where Disperbyk-2150 was the dispersing aid and the values are based on single measurements.

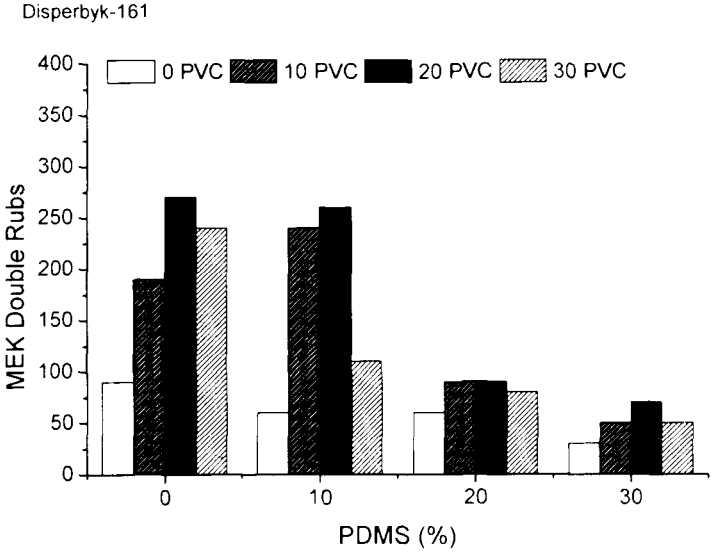

Figure 7.9. MEK Double rubs of siloxane-polyurethane coatings based on PDMS macromers where Disperbyk-161 was the dispersing aid and the values are based on single measurements.

Biofilm retention of *C. lytica* on the pigmented siloxane-polyurethane coatings prepared with PDMS macromers is shown in Figure 7.10. The removal of the bacteria from the surfaces when water jetted at 20 psi for 5 sec is shown in

Figure 7.11. The *C. lytica* biofilm retention on the coatings was similar for all of the experimental coating systems, where the PVC or PDMS binder loading did not affect the biofilm growth on these coatings. The biofilm retention on the experimental coating was reduced compared to the standard coating systems that were tested in parallel. It is important that the inclusion of pigment in these coatings did not cause a drastic increased in biofilm retention, as an increase in attachment would result in more bacteria that must be removed from the coating surface as fouling.

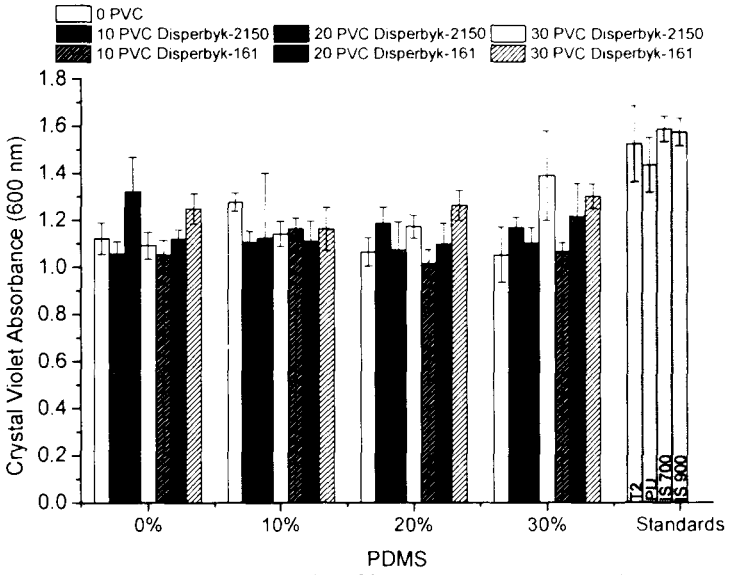

Figure 7.10. *C. lytica* biofilm retention on pigmented siloxane-polyurethane fouling-release coatings prepared with PDMS macromer. The reported values are the means of three measurements and the error bars represent one standard deviation of the means.

The removal of *C. lytica* from the coating surfaces was moderate for most of the experimental coatings, where most coatings showed approximately 50% removal of the attached bacteria. While it's difficult to discern a clear trend based on PDMS content or PVC since the coatings performed very similarly, it is

important to note that the experimental coatings showed as good or better removal of *C. lytica* with water jetting than the standard coating systems. In fact, many of the experimental coating systems showed higher levels of biofilm removal than IS 900, a commercial fouling-release coating.

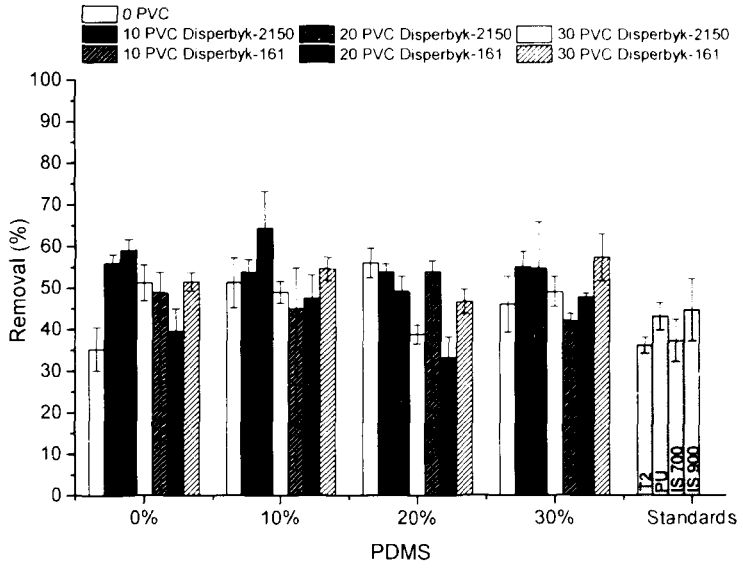

Figure 7.11. Removal of *C. lytica* from pigmented siloxane-polyurethane fouling release coatings prepared with PDMS macromer via water jetting at 20 psi for 5 sec. The reported values are the means of three measurements and the error bars represent one standard deviation of the means.

Biofilm retention of *H. pacifica* on the pigmented siloxane-polyurethane coatings is shown in Figure 7.12. *H. pacifica* showed higher levels of biofilm retention on pigmented coatings, compared to those prepared without pigment. This was especially true when PDMS was included in the binder of the pigmented coatings. However, most of the pigmented systems showed similar levels of bacterial attachment, which was also in the range of the standard coating systems. IS 900 showed the highest levels of biofilm retention for this organisms. While biofilm retention is not indicative of fouling-release performance which is what we

are studying, it does show that coating compositional variables can affect the types and amounts of organisms that choose to settle on surfaces. This may be especially true in natural waters where a wide variety of organisms are present.

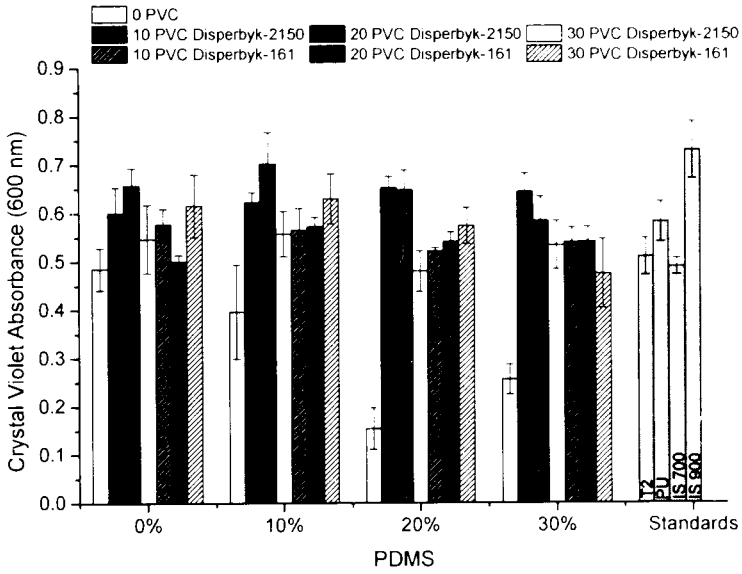

Figure 7.12. *H. pacifica* biofilm retention on pigmented siloxane-polyurethane fouling-release coatings. The reported values are the means of three measurements and the error bars represent one standard deviation of the means.

The removal of *H. pacifica* upon water jetting at 25 psi for 5 sec is shown in Figure 7.13 and indicates that this type of bacteria adheres reasonably well to these coating systems. However, the organism also seemed to adhere well to the commercial fouling-release coatings (IS 700 and IS 900) which also demonstrated only low levels of bacterial removal. Of the standard coating systems, PU showed the highest level of bacterial removal (around 50%). The pigmented polyurethane coatings (0% PDMS) also showed bacterial removal in this range, where 40-60% removal was observed. At 10% and 20% PDMS binder loadings, the removal of *H. pacifica* was slightly reduced compared to the pigmented coatings prepared with

0% PDMS. However, one sample (0 PVC, 30% PDMS) showed approximately 75% removal of the bacteria upon water jetting. Other, pigmented coatings prepared at 30% PDMS showed lower levels of *H. pacifica* removal. While this could indicate an influence of pigmentation on the release properties, further testing would need to be explored before drawing such conclusions and, in general, there did not appear to be a significant change in fouling-release performance brought about by the inclusion of pigment in these systems.

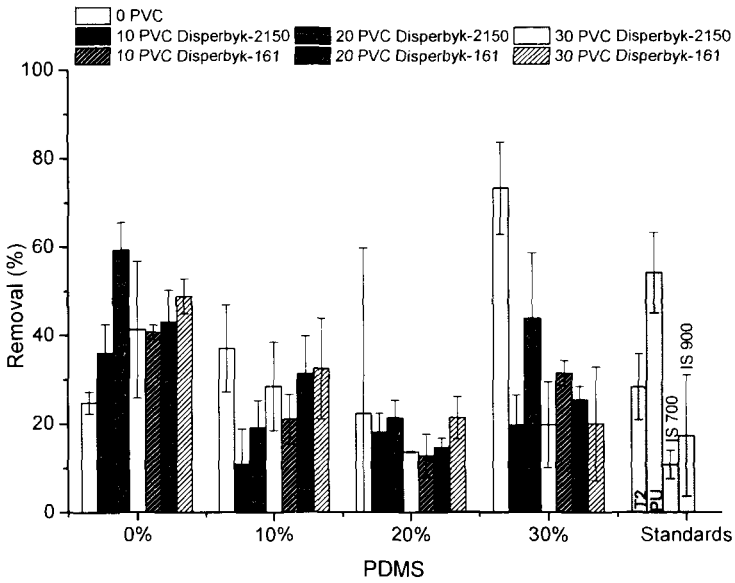

Figure 7.13. Removal of *H. pacifica* from pigmented siloxane-polyurethane fouling release coatings via water jetting at 25 psi for 5 sec. The reported values are the means of three measurements and the error bars represent one standard deviation of the means.

The attachment of *N. incerta* is shown in Figure 7.14. Similar attachment was observed for all of the experimental and standard coatings, suggesting that the PVC or PDMS binder loading did not affect the settlement of diatoms on the coatings. The removal of diatoms from the coating surfaces (Figure 7.15) was lowest for the 0 PVC coating that contained the highest level of PDMS (30%).

However, the pigmented coatings which contained 30% PDMS showed higher removal of diatoms (near 80%) than those prepared with lower levels of PDMS while 0 PVC coatings showed an increase in diatom removal with decreased PDMS content. While conflicting trends are present for the removal of this organism, it is important to note that diatoms are known to adhere well to silicone-based fouling-release coatings.[21,22] The key point in this data set is that pigmentation of these systems did not result in the further reduction of *N. incerta* removal. Rather, an increase in removal was observed with pigmentation, which could aid in the removal of adherent slimes for these types of coatings.

Results from barnacle reattachment on pigmented siloxane-polyurethane coatings based on PDMS macromers are shown in Figure 7.16. For most of the coatings, nearly all of the barnacles were removed from the surfaces without breaking. This indicates that the coatings showed release of shell fouling. However, the removal forces on the experimental coatings were higher than those observed for the standard silicone systems. While the experimental coatings did not show as easy removal of the barnacles, they were still removed without breaking, illustrating the ability of these coatings to provide barnacle release. Coatings prepared at 30% PDMS showed higher barnacle removal forces for pigmented coatings than those prepared at 0 PVC. However, in most cases, the standard deviations of the coatings prepared at 0 PVC overlap with those prepared at 10, 20, and 30 PVC at all levels of PDMS binder loading. While there may be subtle differences between the coatings, this suggests that the values are not statistically significant.

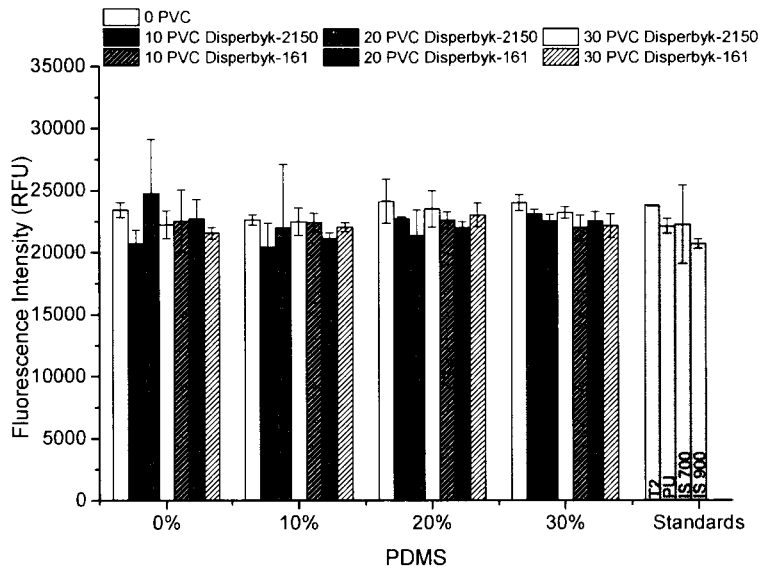

Figure 7.14. Attachment of *N. incerta* on pigmented siloxane-polyurethane fouling-release coatings where the values are the means of three measurements and the error bars represent one standard deviation of the means.

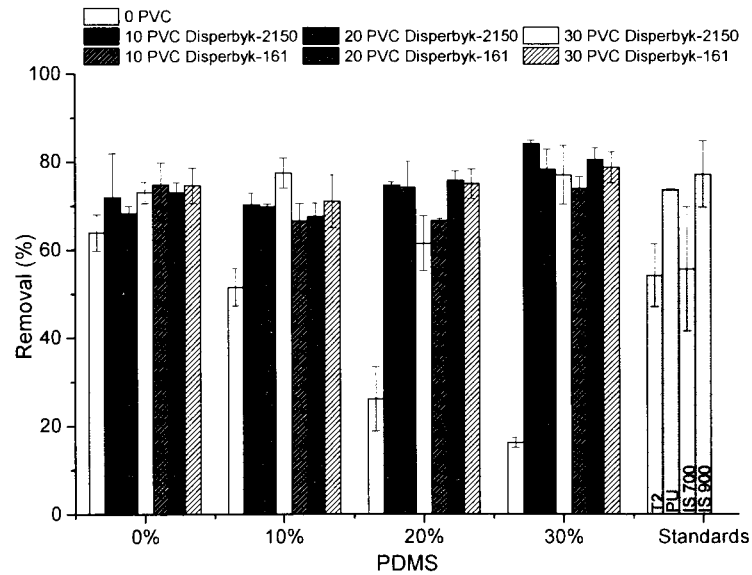

Figure 7.15. Removal of *N. incerta* by water jet (20 psi, 10 sec) from pigmented siloxane-polyurethane fouling-release coatings. The values represent the means of three measurements and the error bars represent one standard deviation of the means.

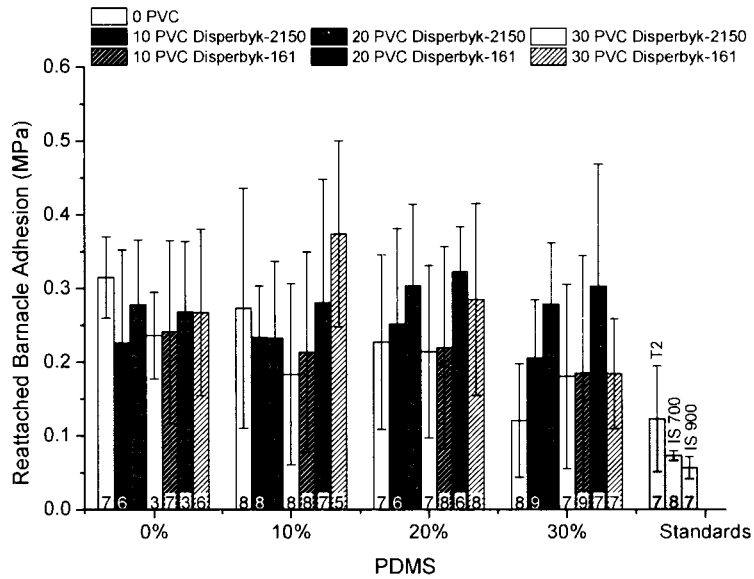

Figure 7.16. Barnacle reattachment on pigmented siloxane-polyurethane fouling-release coatings where the values reported are the means of the number of measurements shown as data labels and the error bars represent one standard deviation of the means.

7.4. Summary and conclusions

Twenty-eight siloxane-polyurethane coatings were prepared to investigate how pigmentation, pigment dispersing aid, and PDMS binder loading influenced overall coating properties and fouling-release performance of these systems. Pigment grinds of TiO_2 in acrylic polyol were prepared using the dispersing aids Disperbyk-2150 and Disperbyk-161. Together with a polyisocayanate resin, and a PDMS macromer, this composed the solid coatings.

The WCA of the coatings increased when PDMS was added to the binder, and the coatings without pigment showed higher water contact angles than that observed for coatings with pigment and the dispersing aid did not seem to affect the WCA. Similar to WCA, the SE of the coatings was affected slightly by

pigmentation of the systems where slightly higher SE was observed when pigment was added to the coatings. Again, the pigment dispersing aid did not play a role. Low PB adhesion was obtained for all of the clear coatings, with all levels of PDMS. However, when pigment was added, higher levels of PDMS were required to achieve the same low PB removal forces. WCA on the top and bottom surfaces of free films confirmed that PDMS had migrated to the coating surfaces when film formation occurred on the substrate. In general, the same initial coating properties were obtained for the pigmented and unpigmented coatings. However, higher levels of PDMS were necessary to obtain the same high WCA, low SE, and low PB adhesion as observed for clear coatings.

The pigmented coatings showed high contrast ratios and good ability to hide a black substrate. Contrast ratios for the films prepared with 10 PVC were slightly lower than those prepared with 20 and 30 PVC which had similar contrast ratios. Gloss of the coatings was reduced with increased PDMS content, especially at high PVC levels. This may have been due to changes in the pigment dispersion stability. The MEK solvent resistance of the coatings was reduced as PDMS was added and increased as the PVC was increased. This reduction in solvent resistance was likely due to reduced crosslink density or increased free volume caused by the inclusion of monofunctional PDMS and the increased solvent resistance with pigmentation was likely caused by the increased diffusion path length for the solvent to enter the coating.

The fouling-release performance of the coatings was analyzed through laboratory bioassays. Removal of *C. lytica* with water jetting was similar for all of

the experimental coatings, and in the range of the standard coatings. *H. pacifica* removal by water jetting was low, and was reduced by the inclusion of PDMS, but was still comparable to the standard commercial fouling-release coatings. Removal of *N. incerta* was high for the pigmented coatings (comparable to FR controls), and low for those which contained 0 PVC showing that pigmentation may increase removal of this organism. Barnacle reattachment showed higher removal forces than observed for the standard coatings, but most of the barnacles were removed during testing without breakage of the barnacle shell which indicates that the coatings exhibited good release of barnacles, even though higher force was required.

In general, the performance of the coatings was not drastically affected by pigmentation. In some cases, the performance of the coatings was improved by pigmentation, as with solvent resistance and removal of *N. incerta* by water jet. In other cases, the properties of the coatings were slightly negatively affected, but the effects were overcome by the incorporation of higher levels of PDMS. To further understand the effects of pigmentation on the fouling-release performance of these systems, field testing is currently underway in the true marine environment. Additional laboratory screening with macroalgae is also underway to determine removal of additional organisms from these pigmented systems.

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CHAPTER 8. SYNTHESIS AND CHARACTERIZATION OF END-FUNCTIONAL PDMS HOMOPOLYMER MOLECULAR BRUSHES BASED ON PDMS MACROMERS

8.1. Introduction

Graft polymers and molecular brushes, are polymeric species which possess polymer chains extending from a polymer backbone.[1,2] These materials are of interest because they are highly tailorable and present countless synthetic possibilities where the polymer backbone and branch composition can be varied, along with the molecular weights of each component, and the density of grafting. Polymer brushes can be prepared from a *grafting through* approach where macromonomers are polymerized, a *grafting from* approach where polymer chains are grown from a central polymer backbone, and a *grafting onto* approach where separately synthesized polymer chains are added to a polymer backbone.[1,2] Figure 8.1 contains an illustration of the differences between the three approaches that can be used in the preparation of molecular brushes.

With the multiple synthetic methods, chemistries and polymer types available for producing molecular polymer brushes, there are seemingly essentially endless possibilities for their synthesis. Reviews on the topic of polymer brushes are available in the literature.[1-5] Polydimethylsiloxane (PDMS) is a common polymer used in the preparation of polymer brushes because of its unique properties such as hydrophobicity, low T_g, high flexibility, low surface energy, biocompatibility, and high thermal stability.[6,7] PDMS has been combined with other polymers such as polystyrene[8,9], poly(ethylene oxide)[10], polysulphone[11], poly(vinyl

alcohol)[12] and poly(methyl methacrylate)[13,14], among others, to form molecular brushes for various applications including drug delivery, membrane formation, and interfacial applications such as polymer blends and solutions.

While polymer brushes are commonly copolymers that are prepared to combine the properties of two polymers, homopolymer brushes have also been synthesized. Homopolymer brushes on surfaces have been extensively explored[5], and the polymerization of macromonomers has also yielded homopolymer brushes.[15-17] PDMS homopolymer molecular brushes have been prepared by the hydrolytic polycondensation of disilyl chloride functional PDMS macromonomers.[18] However, in this preparation, the resulting polymer was essentially a non-functional, branched silicone oil that lacked functionality to participate in additional reactions. Therefore, its use is limited to scenarios such as for lubrication, and when high thermal stability or biocompatibility is required.

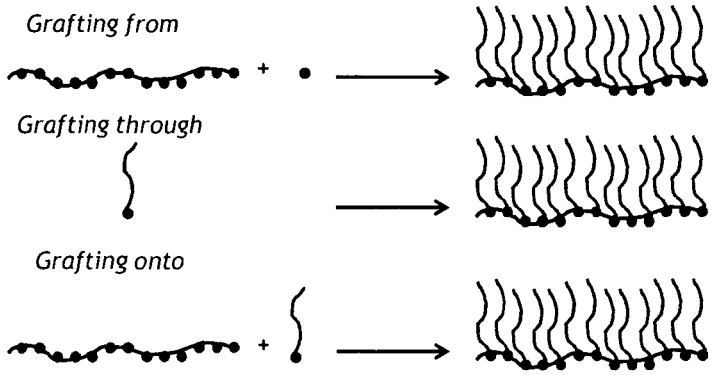


Figure 8.1. Illustration of three approaches that can be used in the preparation of molecular brushes.

In this work, primary amine end-functional PDMS homopolymer molecular brushes were prepared for use in the preparation of siloxane-polyurethane fouling-

release coatings for marine applications. For this application, siloxane-polyurethane coatings have shown promise where the siloxane component has included amine terminated telechelic and monofunctional PDMS.[19,20] The use of PDMS brushes in these types of coatings provided another interesting parameter to explore, where the polymer molecules possess two primary amine groups to react the PDMS into a polyurethane coating, and many branches of PDMS extending from the backbone to provide additional fouling-release performance.

Hydrosilylation is a useful reaction in both organic and organometallic chemistry where a silicon-hydride group adds to a multiple bond, such as a vinyl group.[21] In silicone polymer chemistry, hydrosilylation is commonly used in the coupling of two polymers, and in network formation.[22,23] For this work, hydrosilylation was an obvious synthetic route for the *grafting onto* preparation of PDMS homopolymer molecular brushes because polymers with vinyl and silicon-hydride functionality had been previously prepared. Aminopropyl terminated polydimethylvinyl siloxane (APT-PDMVS) composed the polymer backbone and had pendant vinyl groups which were reacted through hydrosilylation with silicon-hydride groups on monofunctional PDMS macromers (HT-PDMS-M).

Through this synthetic approach, the molecular weight of both the polymer backbone and the polymer grafts, and the density of reactive sites for grafting could be well controlled. Figure 8.2 illustrates the various PDMS molecular brush types that could be prepared using this method by varying the described parameters. Figure 8.3 shows illustrations of the differences of coatings based on PDMS brushes compared to previously prepared siloxane-polyurethane fouling-

release coatings which have shown promising performance. The exploration of PDMS homopolymer brushes was only preliminarily explored in this work. Four PDMS brushes were prepared with different grafting densities, where the polymer backbone and grafting molecular weights were kept constant. The polymers were characterized for completion of reaction and molecular weight. Siloxane-polyurethane coatings were prepared and their water contact angle, surface energy, and pseudobarnacle release were characterized.

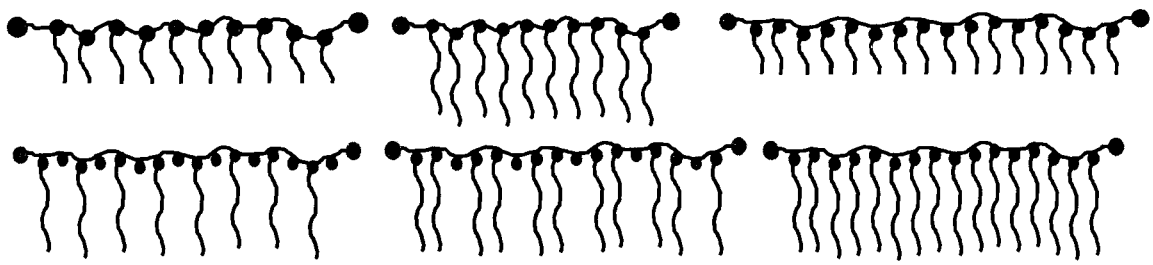


Figure 8.2. PDMS molecular brush types that could be prepared from the hydrosilylation of APT-PDMVS with HT-PDMS-M where the APT-PDMVS and/or HT-PDMS-M molecular weights could be varied, along with the grafting density.

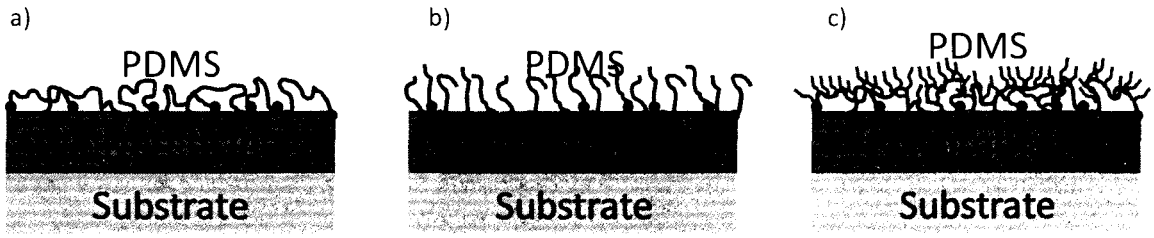


Figure 8.3 Illustrations of siloxane-polyurethane coatings based on telechelic PDMS (a), monofunctional PDMS macromers (b), and homopolymer PDMS brushes (c).

8.2. Experimental

8.2.1. Materials

Hexamethylcyclotrisiloxane (D_3), dimethylchlorosilane (DMCS), octamethylcyclotetrasiloxane (D_4), 1,3,5,7-tetravinyl-1,3,5,7-

tetramethylcyclotetrasiloxanewere (D_4v) and 3-aminopropyl-terminated poly(dimethylsiloxane) (APT-PDMS-875) were purchased from Gelest. Lithium trimethylsilanolate solution (LTMS, 1.0M in dichloromethane), tetrahydrofuran (≥99.9%, inhibitor free and ≥99.9%, 0.025% butylated hydroxyl toluene inhibitor), chloroplatinic acid hexahydrate, molecular sieves (4A beads), benzyltrimethylammonium hydroxide (40% in methanol), acetyl acetone (2,4-pentanedione, PD), methylamyl ketone (MAK), and dibutyltin diacetate (DBTDAc) were received from Sigma-Aldrich. Tolonate IDT 70B (isophorone diisocyanate trimer, IDT, 70% in butyl acetate) was provided generously by Perstorp. Acrylic polyol (50% in toluene) was prepared in-house at NDSU (see previous chapters) All materials were used without further purification.

8.2.2. Monohydride terminated PDMS macromer (HT-PDMS-M) preparation

The synthesis of a 5,000 g mol^{-1} theoretical molecular weight monohydride terminated PDMS macromer (HT-PDMS-M) was prepared as described in previous chapters. The anionic polymerization of D_3 in took place in THF, initiated by LTMS. The 50% mass solution of D_3 (100.42g) was added to a round bottomed flask with activated molecular sieves (7.45g), and sealed with a rubber septum. The solution was degassed for 25 minutes. Following the addition of LTMS solution (12.80g), the polymerization was allowed to proceed at room temperature with magnetic stirring for 2.5 hrs. Termination of polymerization was carried out by the addition of DMCS followed by overnight stirring at room temperature. Rotary evaporation and vacuum filtration were used to isolate the polymer.

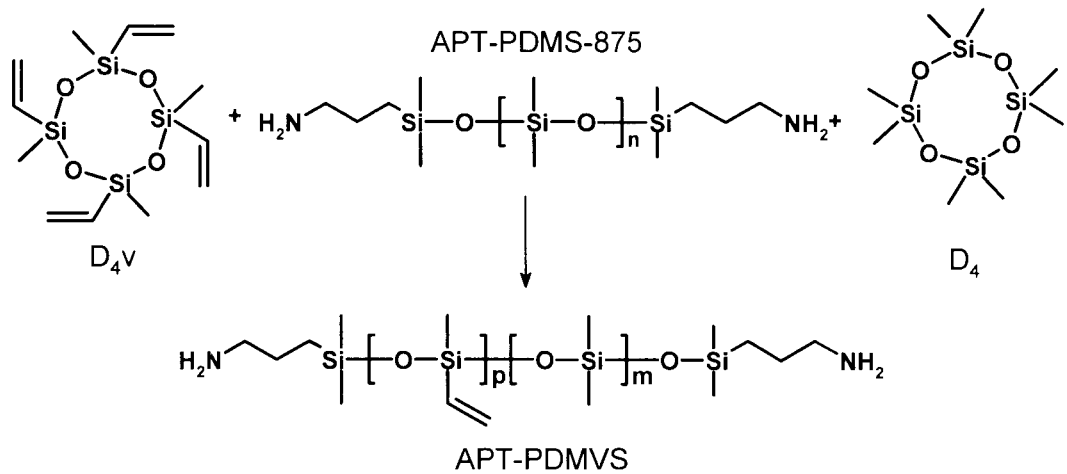
8.2.3. Aminopropyl terminated polydimethylvinylsiloxane (APT-PDMVS) preparation

The two cyclic siloxane monomers D_4 and D_4v were equilibrated in the presence of an amine functional end blocker using anionic ring opening equilibration polymerization to prepare aminopropyl terminated polydimethylvinylsiloxane (APT-PDMVS) with a target molecular weight of 10,000 g mol^{-1} and 1:9 molar ratio of D_4v to D_4. Catalyst solution (benzyltrimethylammonium hydroxide in methanol) was added to D_4 to achieve a 0.1% catalyst concentration based on monomer, and the methanol was removed by rotary evaporation to yield a cloudy mixture. The mixture of D_4 and catalyst (18g), D_4v (2.3g), and APT-PDMS-875 (1.75g) were added to a two neck 250 mL RBF equipped with a magnetic stirrer, condenser, and N_2 inlet. The monomers and end blocker were equilibrated for 48 hrs at 80°C under a nitrogen blanket. Following equilibration, the reaction mixture was heated at 170°C for 45 minutes to decompose the catalyst, yielding a colorless, oily polymer which was characterized by ^{1}H-NMR and GPC. The synthesis of APT-PDMVS is outlined in Scheme 8.1.

8.2.4. End-functional PDMS homopolymer molecular brush preparation

Homopolymer molecular brushes were prepared by the coupling of HT-PDMS-M and APT-PDMVS via hydrosilylation in THF with the catalyst, chloroplatinic acid hexahydrate. Several ratios of vinyl and hydride functional groups were explored (v:h), which are outlined in Table 8.1. To 8 ml glass vials purged with dried N_2, catalyst solution (added as a 5% solution in 2-propanol), APT-PDMVS, and THF were added. The vials were purged with N_2 and the mixtures were stirred for 5 minutes on a magnetic stir plate at room temperature.

The HT-PDMS-M was added, and the vials were purged with N_2 once again, capped and placed in an oil bath and allowed to react for 24 hrs at 65°C with magnetic stirring. The reaction mixtures were removed from the oil bath and analyzed by ^{1}H-NMR and GPC. The preparation of end-functional PDMS homopolymer molecular brushes is outlined in Scheme 8.2. Table 8.1 outlines the composition of the PDMS brushes discussed in this study. Table 8.2 outlines the materials and amounts used in the preparation of the PDMS brushes.



Scheme 8.1. Preparation of 3-aminopropyl terminated PDMVS via equilibration polymerization of D_4 and D_4v.

Table 8.1. End-functional PDMS homopolymer molecular brush composition where the ratio of vinyl to hydride functional groups was varied.

PDMS Brush	PDMS Backbone MW	Branching density	PDMS Branch MW	Vinyl: Hydride Ratio
A	10,000	10%	5,000	1:1
B	10,000	10%	5,000	2:1
C	10,000	10%	5,000	3:1
D	10,000	10%	5,000	1:2

Table 8.2. Materials and amounts used in the preparation of end-functional PDMS homopolymer molecular brushes.

PDMS Brush	Catalyst Solution (g)	APT-PDMVS (g)	THF (g)	HT-PDMS-M (g)
A	0.50	0.50	1.00	3.00
B	0.50	0.50	1.00	1.50
C	0.50	0.50	1.00	1.00
D	0.50	0.25	1.00	3.00

8.2.5. Characterization of polymers

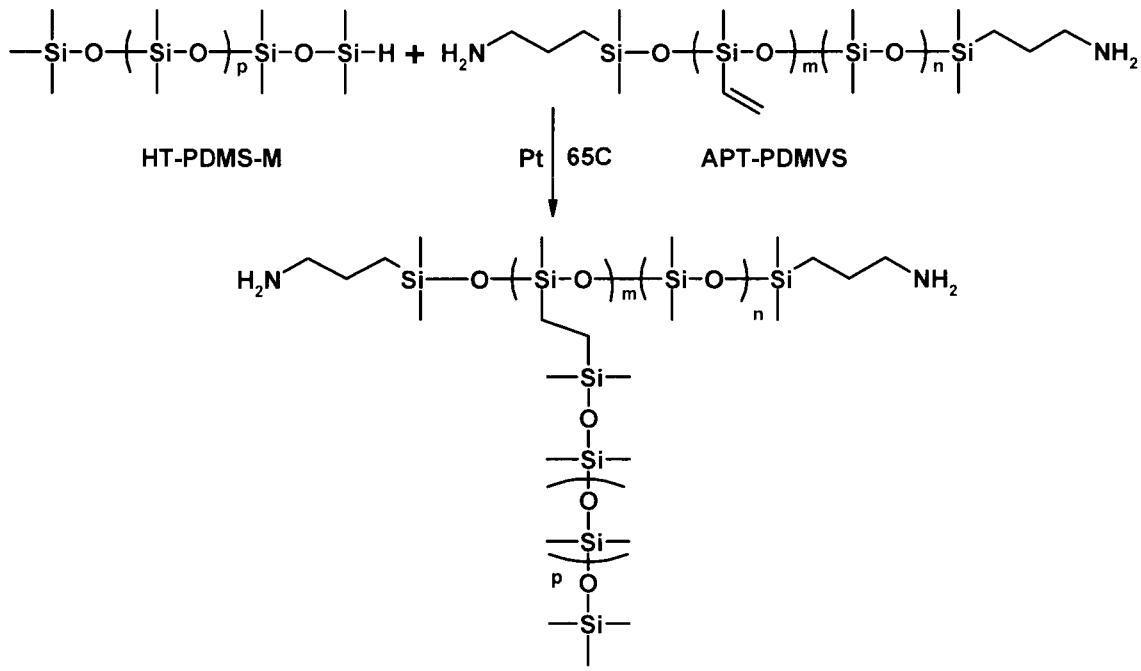
8.2.5.1. NMR spectroscopy: Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained for the polymers using a 400 MHz JEOL ECA400 NMR spectrometer fixed with an autosampler. Samples were prepared at 25 mg ml^{-1} in deuterated chloroform.

8.2.5.2. Symyx Rapid® GPC: High-throughput gel permeation chromatography (GPC) was used to analyze the molecular weight distributions of the linear and brush homopolymers. This analysis was performed relative to polystyrene standards. A polymer concentration of 1-2 mg ml^{-1} in THF and a flow rate of 2.0 mg ml^{-1} were used.

8.2.6. Siloxane-polyurethane coating formulation

Siloxane-polyurethane coatings based on end-functional PDMS homopolymer molecular brushes were prepared with a 1.1:1 ratio of isocyanate functional groups to amine and hydroxyl functional groups. The coating formulations prepared here contained 10% PDMS based on the solid content. The PDMS brush and acrylic polyol were mixed together in a formulation cup, and magnetically stirred overnight at room temperature. The following day, PD was added, followed by IDT and DBTDAc solution. After the addition of each ingredient,

the formulation was shaken to mix and magnetically stirred at room temperature for 5 min. The amounts and materials used in the formulation of siloxane-polyurethane coatings based on PDMS molecular brushes are shown in Table 8.3.



Scheme 8.2. Preparation of amine end-functional PDMS homopolymer molecular brushes via hydrosilylation of hydride terminated PDMS macromers and 3-aminopropyl terminated PDMVS.

8.2.7. Coating preparation and curing

Siloxane-polyurethane coatings were prepared by drawdown onto aluminum panels (3 x 6 in., 0.6 mm thick, type A, alloy 3003 H14, obtained from Q-lab). The coatings were applied using a drawdown bar with an 8 mil gap. Coated panels were ambient cured overnight and oven cured the following day at 80°C for 45 min.

Table 8.3. Reagents and amount used in the preparation of siloxane-polyurethane coatings based on PDMS brushes

PDMS Brush	PDMS Brush (g)	Acrylic polyol (g)	PD (g)	Tolonate IDT 70B (g)	DBTDAc Solution (g)
A	0.71	5.45	0.50	2.54	0.05
B	0.88	5.45	0.50	2.54	0.05
C	1.00	5.45	0.50	2.54	0.05
D	0.74	5.45	0.50	2.54	0.05

8.2.8. Characterization of siloxane-polyurethane coating physical properties

8.2.8.1. Contact angle and surface energy analysis: Contact angle and surface energy (SE) measurements were carried out using a Symyx® Coatings Surface Energy System with First Ten Ångstroms™ software. Three contact angles of water and methylene iodide were measured on the coating surfaces. A photograph was taken with a CCD camera, and automated image analysis was used to measure the wetting angle. The mean contact angles were used to calculate the surface energy of the coatings using the Owens-Wendt method.[24]

8.2.8.2. Pseudobarnacle adhesion: Pseudobarnacle (PB) adhesion measurements were made using a Symyx® Automated Pull-off Adhesion System where the adhesion of an epoxy-glued aluminum stud to the coating surface was measured.[25] The coated panels were placed onto vacuum plates which held them in place for the application of epoxy into designated regions. A plastic template with 24 patches of 7 mm diameter holes was placed over the panels. The two-component epoxy adhesive (Loctite® Hysol® 1C-LV) was mixed and spread over the plastic template using a putty knife. The spreading of the epoxy over the template deposited adhesive through the 7 mm holes of the template, onto the coatings. The panels were placed into clamping jigs with holes which aligned with

the plastic template. Pseudobarnacles were placed in the holes of the clamping jig, atop the epoxy adhesive that was deposited onto the coatings. Six PB were applied to each coating, and weighted foam blocks were placed atop the PB adhesion apparatus to ensure uniform adhesion of the PB to the coatings. The adhesive was allowed to cure overnight. The following day, the weighted foam blocks were removed and the panels (enclosed in clamping jigs) were placed in the automated adhesion system. The PB were removed by an automated pull-off head which applied gradual force, individually to each PB until it was removed from the surface. The force at release was recorded for each PB, and the mean and standard deviation were calculated.

8.3. Results and discussion

Four PDMS homopolymer molecular brushes were prepared via hydrosilylation between pendant vinyl groups in APT-PDMVS and terminal silicon-hydride groups in HT-PDMS-M. Four ratios of vinyl to hydride groups were investigated to explore the influence on polymer properties. The complete reaction of silicon-hydride groups was confirmed by the absence of silicon-hydride peaks in ^{1}H-NMR at 4.7 ppm. In all samples, vinyl peaks remained in the ^{1}H-NMR spectra at 5.7-6.1 ppm following hydrosilylation, although their intensity varied. The spectra are shown in Figure 8.4 where the presence of the silicon-hydride peak was observed in the HT-PDMS-M sample, and the disappearance of this same peak was obvious in the PDMS brush samples. Additionally, a reduction in vinyl peak intensity at 5.7-6.1 ppm was observed in the PDMS brush samples.

GPC was used to investigate the molecular weight of the PDMS brushes, and how they changed with respect to the starting materials. The values obtained from the analysis are shown in Table 8.4. The GPC traces of the polymer brushes are shown in Figures 8.5, 8.6, 8.7, and 8.8 alongside the individual polymers which made up the brushes, and their physical mixture. The GPC traces were similar in all cases of the PDMS brushes, where the PDMS brush produced a broad, single peak. This suggests that a single polymeric species was present with a broader polydispersity than observed for the individual polymers. Additionally, the elution time of the PDMS brushes was longer than that of APT-PDMVS and shorter than HT-PDMS-M. This means that the polymer had a larger hydrodynamic volume than HT-PDMS-M and a smaller hydrodynamic volume than APT-PDMVS. However, the brush was expected to have a larger hydrodynamic volume than the APT-PDMS-M since it is made up of APT-PDMS-M and many macromers. It should be noted that GPC is a relative method for determining molecular weight, and that the molecular weights are relative to polystyrene standards. Furthermore, the molecular configuration in solution could be the cause for such a result where the PDMS brush may be tightly coiled or collapsed upon itself to elute more slowly in GPC compared to the APT-PDMVS.

The results from water contact angle (WCA) and SE analysis for siloxane-polyurethane coatings prepared based on PDMS brushes are shown in Figure 8.9. Figure 8.8 shows that high WCA were obtained for coatings prepared with PDMS brushes, in contrast to a similar coating prepared without PDMS for which a much lower WCA was obtained. The high WCA indicates the presence of PDMS at the

coating surface, as this results in a more hydrophobic surface for and high WCA. The low surface energies of the films prepared with PDMS brushes also indicate the presence of the PDMS at the coating surfaces, where a higher SE was observed for the coating prepared without PDMS.

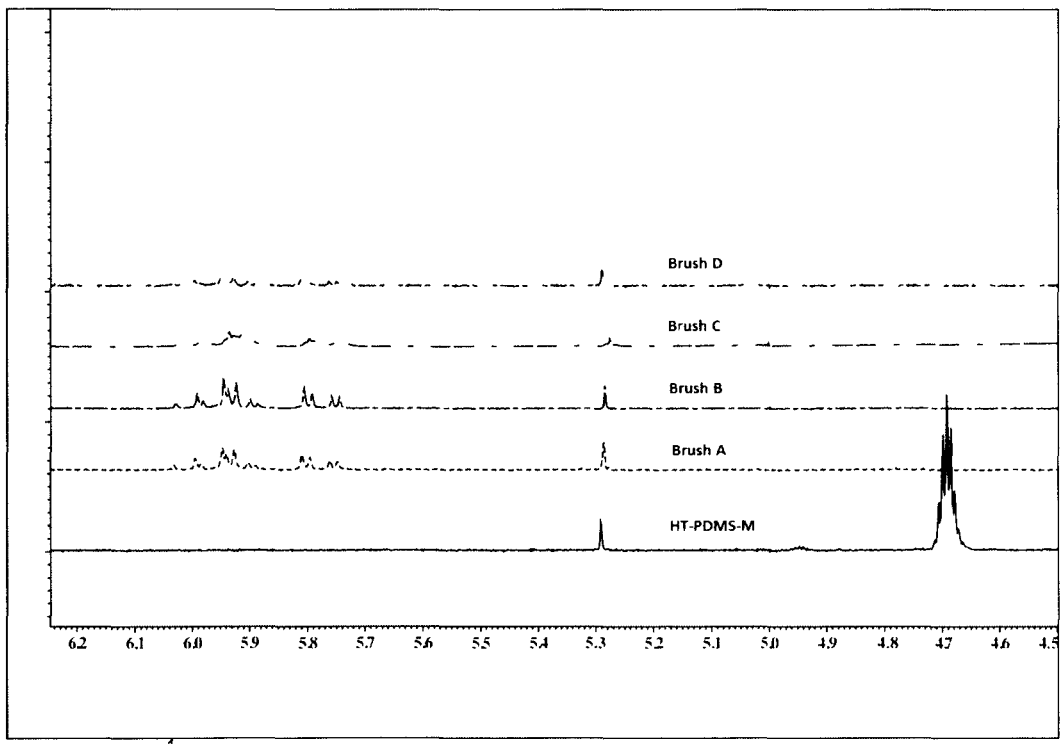


Figure 8.4. ^{1}H-NMR spectra of PDMS brushes and HT-PDMS-M where the disappearance of silicon-hydride peaks can be observed at 4.7 ppm and a reduction in vinyl peak intensity can be observed at 5.7-6.1 ppm.

The results from PB adhesion on the coatings prepared with PDMS brushes are shown in Figure 8.10. The PB adhesion for the coatings prepared with PDMS brushes was lower than that obtained for a coating prepared without PDMS. This indicates the potential of these coatings to serve as release coatings, where their presence reduces the interfacial adhesion between the epoxy adhesive and the coating. Slightly higher PB

adhesion was obtained for coatings prepared with PDMS brushes A and D, compared to B and C, even though the same level of PDMS was used in all of the coatings.

Table 8.4. Numerical results from GPC screening

Sample	$\overline{M_n}$	$\overline{M_w}$	PDI
HT-PDMS-M	3,800	4,400	1.17
APT-PDMVS	12,900	21,200	1.63
Physical Mixture HT-PDMS-M and APT-PDMVS	3400	7200	2.1
PDMS Brush A	4400	6700	1.52
PDMS Brush B	4200	6800	1.61
PDMS Brush C	3700	6200	1.66
PDMS Brush D	5100	7900	1.54

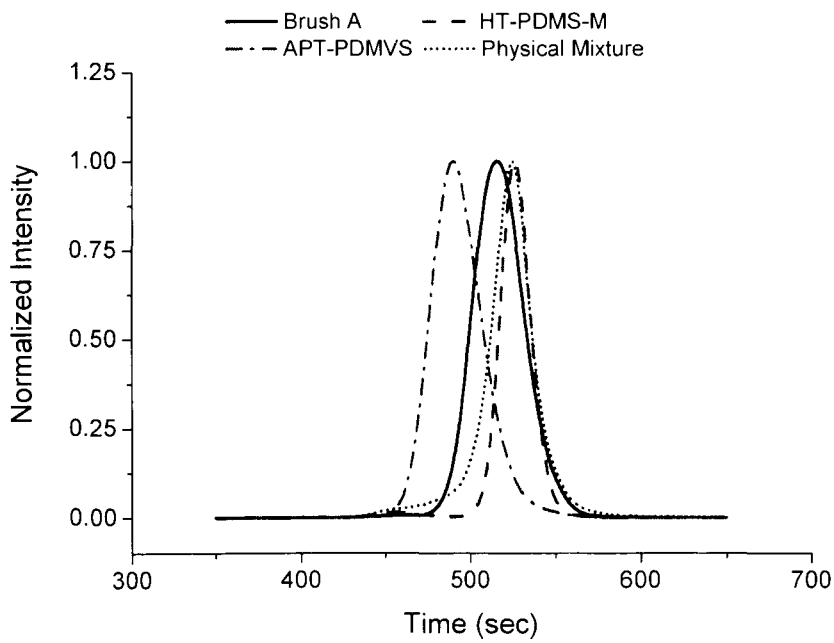


Figure 8.5. GPC trace of PDMS Brush A with HT-PDMS-M, APT-PDMVS, and a physical mixture of HT-PDMVS and APT-PDMVS.

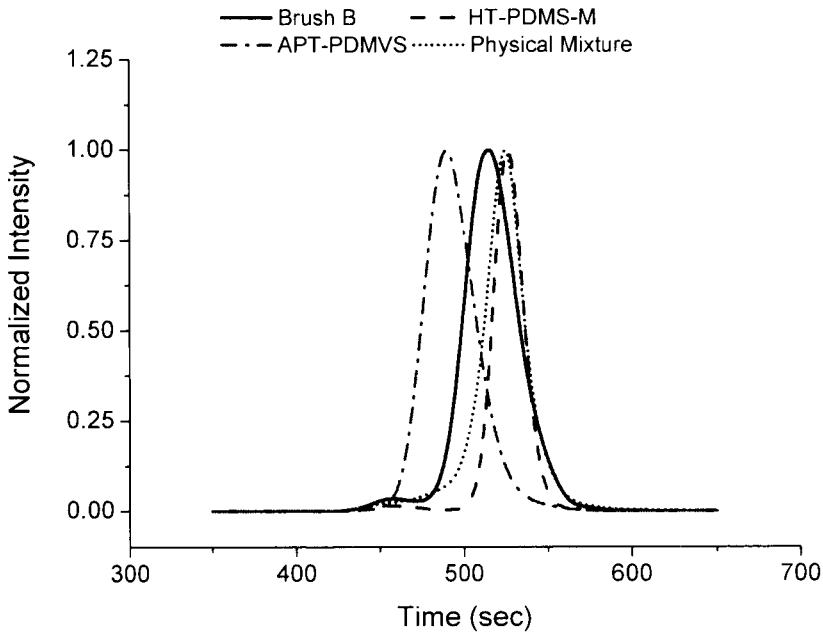


Figure 8.6. GPC trace of PDMS Brush B with HT-PDMS-M, APT-PDMVS, and a physical mixture of HT-PDMVS and APT-PDMVS.

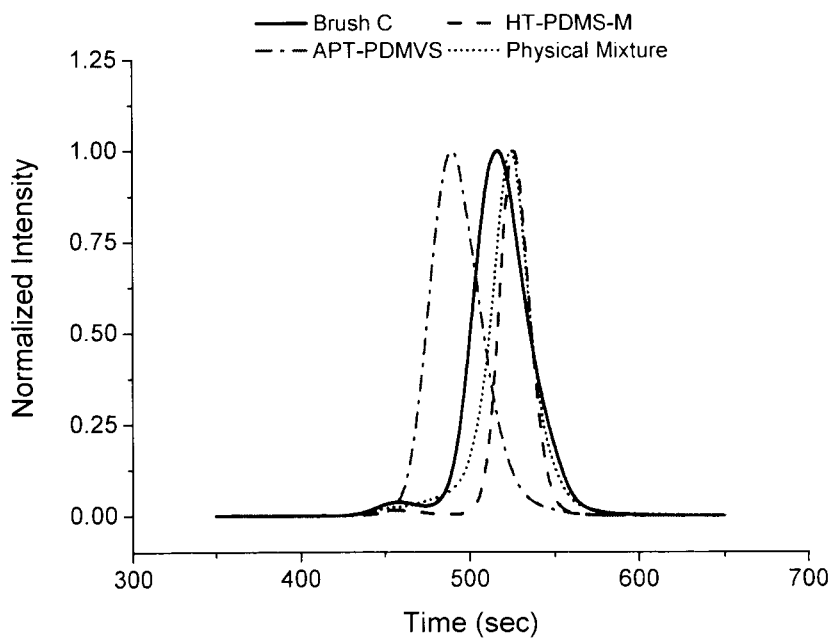


Figure 8.7. GPC trace of PDMS Brush C with HT-PDMS-M, APT-PDMVS, and a physical mixture of HT-PDMVS and APT-PDMVS.

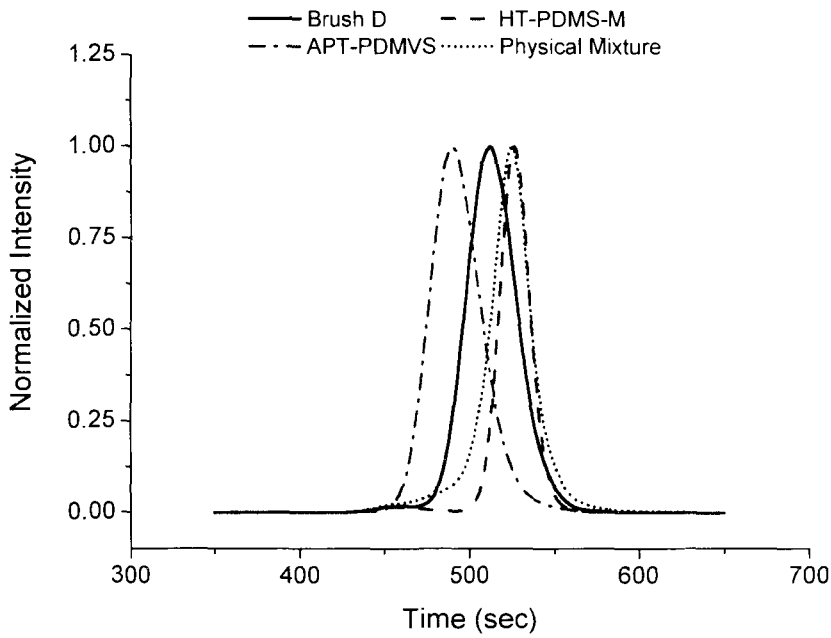


Figure 8.8. GPC trace of PDMS Brush D with HT-PDMS-M, APT-PDMVS, and a physical mixture of HT-PDMVS and APT-PDMVS.

The differences observed in PB adhesion were unexpected and are difficult to explain because low SE was obtained for all coatings and this generally correlates to low PB removal force. Based on the ratios of silicon-hydride functionality to vinyl functionality, the PDMS brushes with the lowest density of grafting provided better PB release properties. This result may be related to polymeric differences that have influenced the rate at which PDMS migrated to the surface. If the PDMS brushes are considered as cylindrical polymers, those with fewer grafts may resemble a smaller polymer "cylinder", as the grafts can easily lie against the main backbone. In more heavily grafted brushes, the grafted polymers will be forced to extend away from the backbone, resulting in a larger polymer "cylinder". This concept is the basis for polymer brush morphology, where high

density of grafting is known to force grafts to extend outward from the polymer backbone instead of relaxing. Perhaps the difference in the size of polymer "cylinders" is the cause for differences in release properties. However, the differences in grafting density presented here are small compared to polymer brushes which may have grafting at every polymer repeat unit. Further experimentation is required to better understand the true cause for these differences in release performance, especially when the WCA and SE of all of the coatings were very similar.

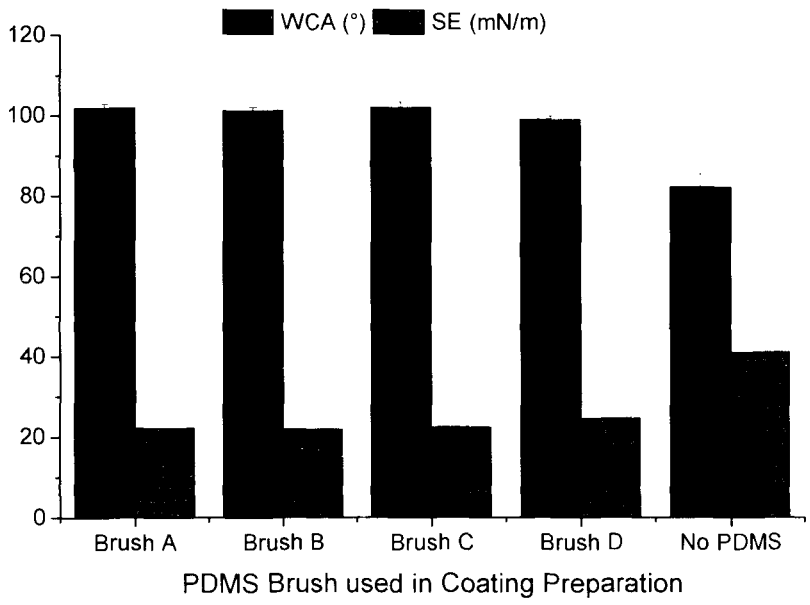


Figure 8.9. Water contact angle (WCA) and surface energies (SE) of the siloxane-polyurethane coatings prepared with PDMS brushes. For WCA, the reported values are the means of three measurements and the error bars represent one standard deviation of the mean. SE was calculated by the Owens-Wendt method using the mean values from WCA and methylene iodide contact angle analysis.

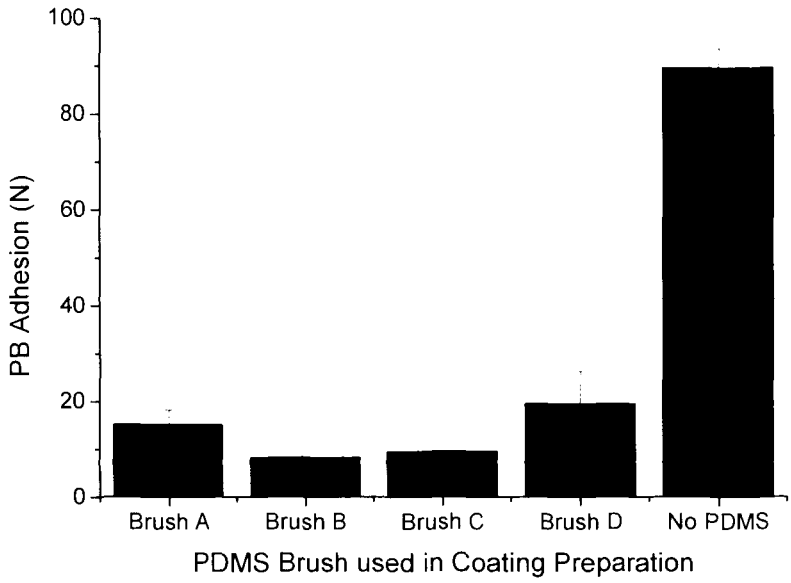


Figure 8.10 PB adhesion on siloxane-polyurethane coatings prepared with PDMS brushes where the values are the means of six measurements and the error bars represent one standard deviation of the mean.

8.4. Summary and conclusions

In this chapter, the preparation and characterization of end-functional PDMS homopolymer molecular brushes was described. Four PDMS brushes were prepared with different polymer grafting densities, based on the ratios of vinyl to silicon-hydride functional groups. The brush polymers were characterized by Rapid® GPC to compare the molecular weight and molecular weight distributions with the "parent" polymers, and by ^{1}H-NMR to confirm complete reaction of the silicon-hydride functional groups during hydrosilylation. The amine-functional PDMS brushes were formulated into siloxane-polyurethane coatings for initial screening as fouling-release coatings. It was found that the PDMS brush synthesis

was successful, and that their incorporation into siloxane-polyurethane coatings increased WCA, decreased SE, and caused a reduction in PB adhesion.

The work presented in this chapter is the preliminary preparation and assessment of these polymers for use in fouling-release marine coatings. Future generations of polymers should be further characterized and screened to analyze the exact molecular weight and molecular weight distributions by methods such as matrix assisted laser desorption/ionization spectroscopy (MALDI). Additional screening of fouling-release performance also needs to be completed to better understand the release performance of coatings based on PDMS brushes. Laboratory biological screening assays are useful tool for this, and preparation of these coatings for this type of analysis is already underway.

The use of these types of polymers could be expanded beyond marine coatings, where they may find utility in the preparation of biomedical devices, interpenetrating polymer networks, drug delivery, or even gas permeation membranes. Other routes of preparing these interesting polymers could also be explored, depending on the final application. For example, the polymerization of acrylate or methacrylate terminated PDMS macromers could be easily accomplished (*grafting through*) to prepare molecular brushes. Other synthetic approaches such as the use of thiol-ene chemistry could be explored as an alternative *grafting onto* preparation. Polymer brushes with different functionalities on the chain ends could also be prepared for various applications, by reaction of the amine group, or by the use of a different end-blocker during preparation of the polymer backbone. The preparations of similar types of polymer brushes are

endless, and their functionality improves utility in combining chemistries, and incorporating brushes into polymer networks.

8.5. References

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CHAPTER 9. SYNTHESIS AND CHARACTERIZATION OF BRANCHED PDMS MACROMERS

9.1. Introduction

Marine biofouling is an expensive problem that is estimated to cost the US Navy $1 billion per year.[1] These expenses are due to reduced ship performance from increased hydrodynamic drag that the accumulation of biofouling causes (i.e. increased fuel consumption and more frequent dry docking intervals).[2-4] Environmental concerns also arise from biofouling, as antifouling (AF) paints that repel biofouling organisms by the inclusion of biocides have been found to leach toxic ingredients into the marine environment which been found to negatively affect organisms that do not cause biofouling.[5] Additionally, the transfer of non-native organisms by biofouling attachment and subsequent release has led to even greater concerns with the ecological introduction of species.[6,7]

Because of the expenses induced by biofouling, the Navy and other ship users need an effective method of controlling biofouling. Until recently, this had been accomplished primarily through the use of toxic AF paints. In light of their recent negative, environmental profile, the development of non-toxic alternatives, such as fouling-release (FR) coatings has become heavily researched. These systems operate differently than AF coatings, as they offer a low surface energy surface on which organisms have difficulty attaching and can be easily removed.[8] Most of these types of coatings have been based on silicone elastomers which are fairly effective, but are soft, become easily damaged, and have poor adhesion to

marine primers.[9] Therefore, siloxane-polyurethane FR coatings have been recently explored as alternatives to traditional elastomer based FR coatings.[10]

Siloxane-polyurethane FR coatings are a class of self-stratified coatings where the inclusion of a reactive polydimethylsiloxane (PDMS) is used to modify an exterior polyurethane coating. When mixed together and applied to a surface, the PDMS component migrates to the coating surface due to its low surface energy and its general incompatibility with the polyurethane bulk.[11] Because of its reactive nature, however, the PDMS becomes permanently anchored to the polyurethane bulk, and coatings with a tough and durable polyurethane bulk and a low surface energy surface result, which are stable in water due to their crosslinked nature.[12] Siloxane-polyurethane coatings have been explored based on reactive PDMS species that have included telechelic PDMS and linear PDMS macromers.[13,14] The use of PDMS macromers have shown promise in the development of siloxane-polyurethane coatings, as has been shown in previous chapters of this thesis. However, thus far, the exploration of these types of macromers has been limited to linear macromers, and the use of different macromer architectures may provide additional interesting properties.

In this work, the synthesis and characterization of branched PDMS macromers and their incorporation into siloxane-polyurethane coatings is discussed. A schematic of how these macromers may be used in the preparation of these coatings is shown in Figure 9.1 where a) shows the general self-stratified siloxane-polyurethane coating, and b) shows how a linear, double branched and triple branched PDMS macromer may be incorporated into the coating system.

The preparation of these macromers from hydrosilylation of hydride terminated PDMS macromers (HT-PDMS-M) with allyl ethers and the chemical reduction of nitrile terminated PDMS macromers (CN-PDMS-M) to amine terminated PDMS macromers will be discussed.

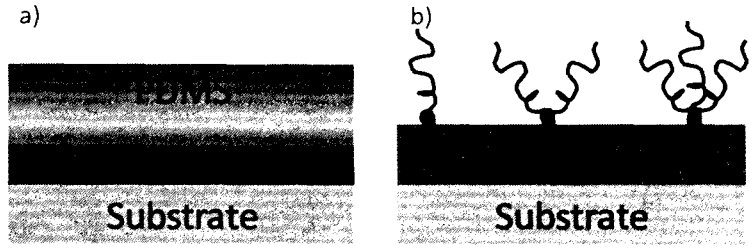


Figure 9.1. Siloxane-polyurethane coatings where a) is an illustration of the self-stratification of the coatings and b) is an illustration of the possibilities when linear or branched PDMS macromers are used in these systems.

9.2. Experimental

9.2.1. Materials

Hexamethylcyclotrisiloxane (D_3), dimethylchlorosilane (DMCS), 3-cyanopropyldimethylchlorosilane (CP-DMCS), 3-cyanopropylmethyldichlorosilane (CP-MDCS), 3-cyanopropyltrichlorosilane (CP-TCS), and Karstedt catalyst solution (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, 2.1-2.4% Pt in xylene) were purchased from Gelest. Lithium trimethylsilanolate solution (LTMS, 1.0M in dichloromethane), tetrahydrofuran (≥99.9%, inhibitor free and ≥99.9%, 0.025% butylated hydroxyl toluene inhibitor), chloroplatinic acid hexahydrate, molecular sieves (4A beads), allyloxyethaneol, acetyl acetone (2,4-pentanedione, PD), methylamyl ketone (MAK), dibutyltin diacetate (DBTDAc), lithium aluminum hydride, and sodium borohydride were received from Sigma-Aldrich. Tolonate IDT

70B (isophorone diisocyanate trimer, IDT, 70% in butyl acetate), trimethylolpropane monoallyl ether (TMPME, 98% monoallyl ether), trimethylolpropane diallyl ether (TMPDE 90, minimum 90% diallyl ether), and allylpentaerythritol (APE, 75-84% triallyl ether) were provided generously by Perstorp. Acrylic polyol (50% in toluene) was prepared in-house at NDSU (see previous chapters). All materials were used without further purification.

9.2.2. Preparation and characterization of branched PDMS macromers from allyl ethers

9.2.2.1. Polymerization of hydride terminated PDMS macromers: The polymerization of hydride terminated PDMS macromers (HT-PDMS-M) has been described in previous chapters. In this case, the target molecular weight of the PDMS macromer was 5,000 g/mol. To a sealed round bottom flask (RBF) containing a degassed solution of D_3 in THF (50% mass), LTMS solution in dichloromethane was added to initiate polymerization at room temperature. The polymerization was allowed to proceed for 24 hr. Termination of polymerization was carried out by the addition of 100% molar excess DMCS at 2-5°C. The reaction mixture was stirred and allowed to gradually warm to room temperature over several hours. The amounts of reagents that were used for the preparation of HT-PDMS-M are shown in Table 9.1.

Table 9.1. Reagent amounts used in the polymerization of HT-PDMS-M

	D_3		LTMS soln	LTMS		DMCS	
Theoretical MW (g mol^{-1})	Mass (g)	mmol	Mass (g)	Mass (g)	mmol	Mass (g)	mmol
5,000	147.2	662	39.1	2.94	30.6	10.0	105

9.2.2.2. Hydrosilylation of HT-PDMS-M with allyl ethers: The preparation of branched PDMS macromers from allyl ethers (BAE-PDMS-M) was carried out via hydrosilylation of HT-PDMS-M with hydroxyl functional allyl ethers. Structures of the allyl ether compounds used in this preparation are shown in Figure 9.2. The PDMS and stoichiometric amounts of allyl ether were dissolved in toluene at a concentration of 30% solids. The solutions were degassed by bubbling N_2 through each solution for 15 min. Hydrosilylation was carried out at 60°C in the presence of Karstedt catalyst. The reactions were run for 77 hours in 25-27 hour increments, but a peak remained at 4.7 ppm in ^{1}H NMR, representing the silicon-hydride functional group. Therefore, an excess of allyl ether was added and the reactions were run for 25 hours at 60°C. The reaction of silicon-hydride functional groups had completed and the peak at 4.7 ppm had disappeared, but residual allyl peaks remained (5.2 ppm, 5.9 ppm). Table 9.2 summarizes the amounts of reagents used for the hydrosilylation reactions, with and without the addition of excess allyl ether. Scheme 9.1 shows the reaction schemes for the functionalization of the branched PDMS macromers via hydrosilylation of allyl ethers with HT-PDMS-M. The solvent was removed from the samples using rotary evaporation. The macromers were extracted several times with methanol to remove color and to remove unreacted ally ether polyol.

9.2.2.3. Symyx® Rapid® GPC: High-throughput gel Permeation Chromatography (GPC) was used to analyze the molecular weight distributions of the linear and branched PDMS macromers. This analysis was performed relative

to polystyrene standards. A polymer concentration of 1-2 mg ml^{-1} in THF and a flow rate of 2.0 mg ml^{-1} were used.

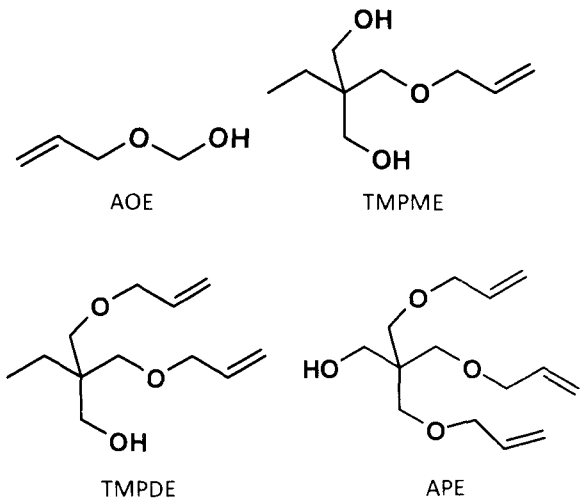
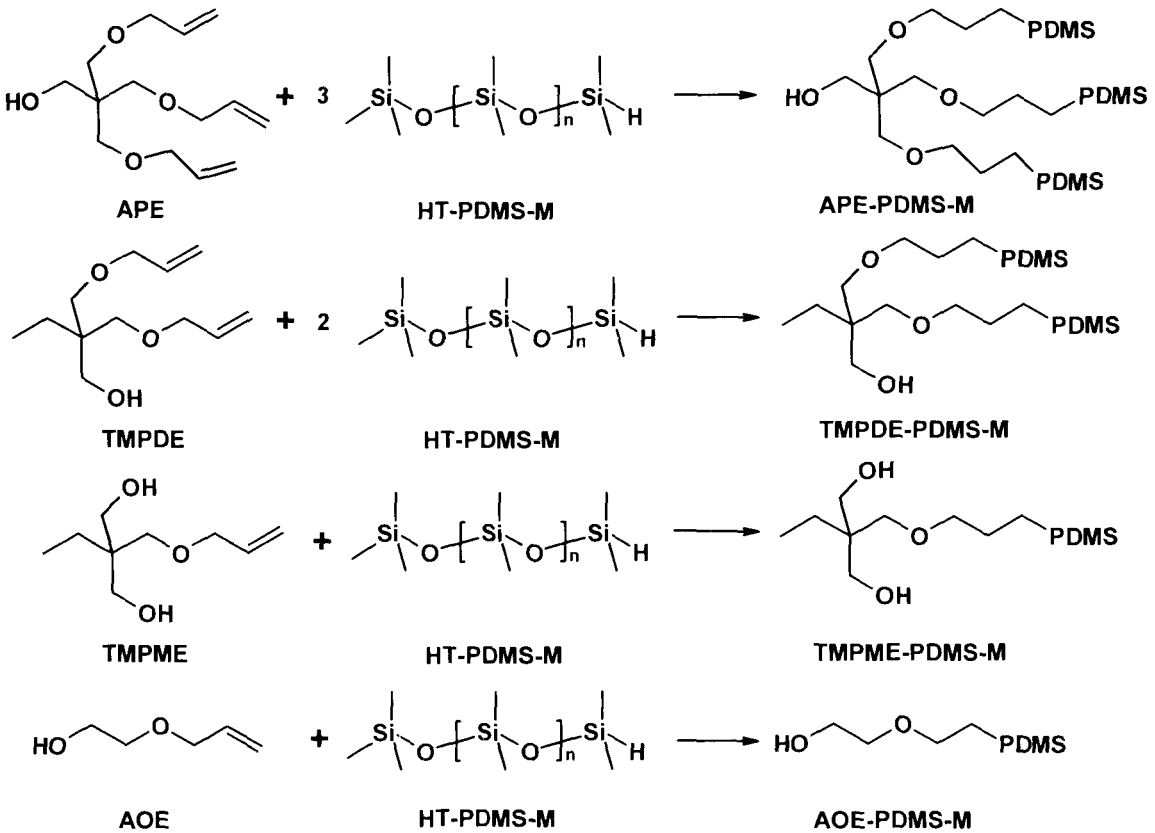


Figure 9.2. Structures of allyl ethers used in the preparation of branched PDMS macromers

9.2.2.4. NMR spectroscopy: Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR) spectroscopy was performed using a Jeol 400 MHz spectrometer fixed with an autosampler. Solutions were prepared at 25 mg ml^{-1} in deuterated chloroform. Sixteen scans were performed with a 0.3 sec delay time.

Table 9.2. Reagents and amounts used in the hydrosilylation of allyl ethers with HT-PDMS-M

Allyl ether						HT-PDMS-M		Toluene
Type	MW (g mol^{-1})	Mass (g)	mmol	Excess (g)	Excess (mmol)	Mass (g)	mmol	Mass (g)
TMPME	174.3	0.34	1.93	1.50	8.61	9.66	1.93	23.33
APE	256.4	0.17	0.66	1.50	5.85	9.83	1.97	23.33
TMPDE	213.3	0.21	0.98	1.50	7.03	9.79	1.96	23.33
AOE	102.1	0.20	1.96	1.50	14.69	9.80	1.96	23.33



Scheme 9.1. Hydrosilylation of allyl ethers with HT-PDMS-M used in the preparation of branched PDMS macromers

9.2.3. Preparation and characterization of siloxane-polyurethane coatings based on branched PDMS macromers from allyl ethers

9.2.3.1. Siloxane-polyurethane coating formulation: Siloxane-polyurethane coating formulations were prepared using BAE-PDMS-M, IDT, PCL polyol, DBTDAc, and PD. The coatings were formulated with a 1.1:1 ratio of isocyanate to hydroxyl equivalents, accounting for both the BAE-PDMS-M and the polyol. The coating formulations are outlined in Table 9.3 with reagent quantities for approximately 10 grams of total formulation. The coating formulations were prepared by first mixing the PDMS macromers with the PCL polyol (90% in MAK)

overnight. The following day, the PD was added and the formulation was mixed. The addition of IDT (70% in butyl acetate) and DBTDAc solution (1% in MAK) followed, and the formulation was shaken to mix and then magnetically stirred at room temperature.

Table 9.3 Materials and amounts used in the preparation of siloxane-polyurethane coatings based on BAE-PDMS-M

Coating ID	PDMS (g)	PCL polyol Solution (g)	PD (g)	Tolonate IDT 70B (g)	DBTDAc Solution
TMPE-PDMS-M-10%	0.75	2.39	0.98	6.57	0.11
TMPE-PDMS-M-5%	0.38	2.54	0.99	6.91	0.11
TMPE-PDMS-M-1%	0.08	2.66	1.00	7.18	0.11
APE-PDMS-M 10%	0.75	2.39	0.98	6.57	0.11
APE-PDMS-M -5%	0.38	2.54	0.99	6.91	0.11
APE-PDMS-M-1%	0.08	2.66	1.00	7.18	0.11
TMPDE-PDMS-M-10%	0.75	2.39	0.98	6.57	0.11
TMPDE-PDMS-M-5%	0.38	2.54	0.99	6.91	0.11
TMPDE-PDMS-M-1%	0.08	2.66	1.00	7.18	0.11
AOE-PDMS-M-10%	0.75	2.39	0.98	6.57	0.11
AOE-PDMS-M-5%	0.38	2.54	0.99	6.91	0.11
AOE-PDMS-M-1%	0.08	2.66	1.00	7.18	0.11

9.2.3.2. Siloxane-polyurethane coating application and curing: The coating compositions are outlined on the basis of resins solids in Table 9.4. Coatings were applied to bare aluminum panels (3 x 6 in., 0.6 mm thick, type A, alloy 3003 H14, obtained from Q-lab) using a drawdown bar with an 8 mil gap. The coatings were ambient cured overnight and oven cured the following day at 80°C for 45 min.

Table 9.4. Solid coating composition of siloxane-polyurethane coatings based on BAE-PDMS-M

	Mass % of Solids				
Coating ID	PDMS	IDT	PCL polyol	Total Solids	DBTDAc
TMPE-PDMS-M-10%	10%	61%	29%	76%	0.015%
TMPE-PDMS-M-5%	5%	65%	30%	75%	0.015%
TMPE-PDMS-M-1%	1%	67%	32%	75%	0.015%
APE-PDMS-M 10%	10%	61%	29%	76%	0.015%
APE-PDMS-M -5%	5%	65%	30%	75%	0.015%
APE-PDMS-M-1%	1%	67%	32%	75%	0.015%
TMPDE-PDMS-M-10%	10%	61%	29%	76%	0.015%
TMPDE-PDMS-M-5%	5%	65%	30%	75%	0.015%
TMPDE-PDMS-M-1%	1%	67%	32%	75%	0.015%
AOE-PDMS-M-10%	10%	61%	29%	76%	0.015%
AOE-PDMS-M-5%	5%	65%	30%	75%	0.015%
AOE-PDMS-M-1%	1%	67%	32%	75%	0.015%

9.2.3.3. Pseudobarnacle (PB) adhesion: Pseudobarnacle adhesion measurements were made using a Symyx® Automated Pull-off Adhesion System where the adhesion of an epoxy-glued aluminum stud to the coating surface was measured.[15] The coated panels were placed onto vacuum plates which held them in place for the application of epoxy into designated regions. A plastic template with 24 patches of 7 mm diameter holes was placed over the panels. The two-component epoxy adhesive (Loctite® Hysol® 1C-LV) was mixed and spread over the plastic template using a putty knife. The spreading of the epoxy over the template deposited adhesive through the 7 mm holes of the template, onto the coatings. The panels were placed into clamping jigs with holes which aligned with the plastic template. Pseudobarnacles were placed in the holes of the clamping jig, atop the epoxy adhesive that was deposited onto the coatings. Six PB were applied to each coating, and weighted foam blocks were placed atop the PB

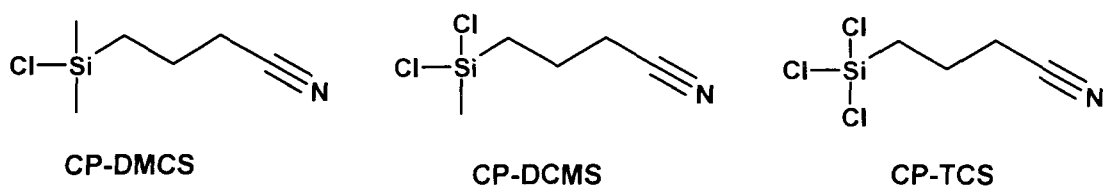
adhesion apparatus to ensure uniform adhesion of the PB to the coatings. The adhesive was allowed to cure overnight. The following day, the weighted foam blocks were removed and the panels (enclosed in clamping jigs) were placed in the automated adhesion system. The PB were removed by an automated pull-off head which applied gradual force, individually to each PB until it was removed from the surface. The force at release was recorded for each PB, and the mean and standard deviation were calculated.

9.2.3.4. Contact angle and surface energy analysis: Contact angle and surface energy (SE) measurements were carried out using a Symyx® Coatings Surface Energy System with First Ten Ångstroms™ software. Three contact angles of water and methylene iodide were measured on the coating surfaces. A photograph was taken with a CCD camera, and automated image analysis was used to measure the wetting angle. The mean contact angles were used to calculate the surface energy of the coatings using the Owens-Wendt method.[16]

9.2.4. Preparation, reduction and characterization of nitrile terminated branched PDMS macromers

9.2.4.1. Polymerization of nitrile terminated PDMS macromers (CN-PDMS-M): The polymerization of nitrile terminated PDMS macromers was carried out similarly to that of HT-PDMS-M, with the same linear target molecular weight of 5,000 g/mol. A solution of D_3 in THF was measured into a N_2 purged RBF. The RBF was sealed with a rubber septum and the D_3 solution was degassed by bubbling N_2 through the solution for 15 min. Addition of LTMS solution was carried out through the rubber septum to maintain the closed environment, and the

polymerization was allowed to proceed to 3 hr with stirring at room temperature. A nitrile functional chlorinated silane compound was added to the sealed RBF to terminate the polymerization. The materials and amounts used in the polymerization of CN-PDMS-M is shown in Table 9.5. The terminating species used in this preparation are shown in Figure 9.3. Up to three chlorine groups were present on the silicon atom in the terminating species and, therefore, up to three living PDMS chains could be terminated with a single molecule (i.e. the number of PDMS chains which added to the terminating species was determined by the number of chlorine atoms present). After the addition of the terminating species, the reaction mixtures were allowed to stir at room temperature overnight to allow all of the polymer chain ends to react with the terminating species. The termination of living PDMS chains with nitrile functional chlorinated silane compounds is shown in Scheme 9.2.



CP-DMCS **CP-DCMS** **CP-TCS**

Figure 9.3. Nitrile functional chlorinated silane terminating agents used in the preparation of CN-PDMS-M

9.2.4.2. Reduction of nitrile functional groups with lithium aluminum hydride:

The reduction of nitrile terminated PMDS macromers with lithium aluminum hydride ($LiAlH_4$) was carried out at room temperature with magnetic stirring, in inhibitor-free THF, in a nitrogen (N_2) glove box for 3 hr. $LiAlH_4$ pellets were pulverized in the N_2 glove box and measured into vials. A solution of CN-PDMS-M

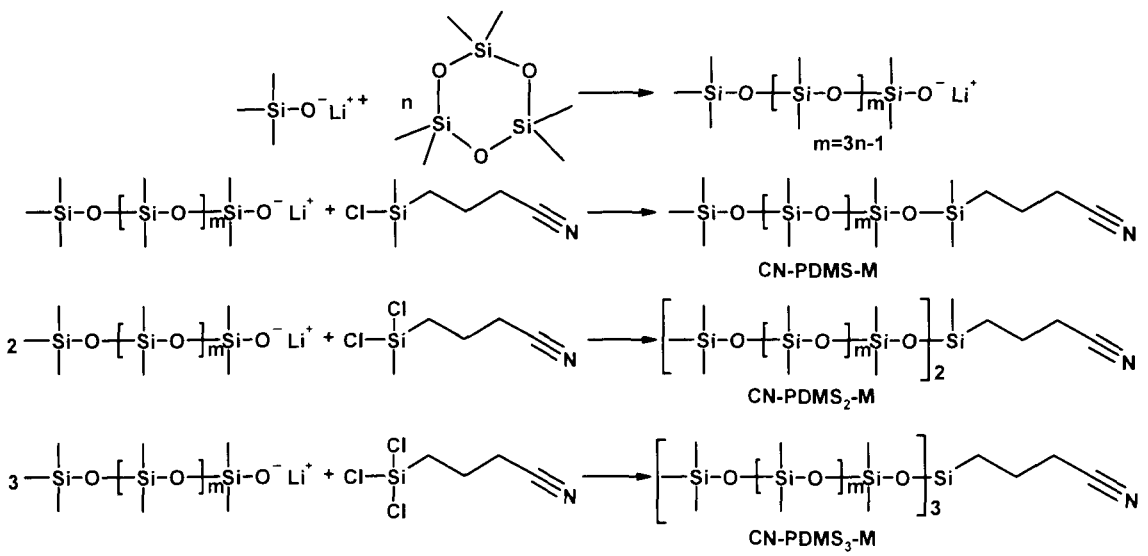
(25% in THF) was added dropwise to the $LiAlH_4$ powder. After the 3 hr reaction time had passed, the reaction mixture was quenched by the dropwise addition of deionized water. Gas (hydrogen) evolved during the quenching stage, and the addition of water was halted when the gas evolution ceased. The reaction mixtures were left stirring overnight at room temperature, in the N_2 glove box. Rotary evaporation and filtration were used to isolate the polymer. Four stoichiometric ratios of CN-PDMS-M were attempted to determine the amount of $LiAlH_4$ necessary for reduction of the nitrile functional group to an amine and to determine whether the reducing agent affected the molecular weight of the polymer. The reagents and amount used in the reduction of nitrile groups on CN-PDMS-M with $LiAlH_4$ are shown in Table 9.6.

Table 9.5. Materials and amounts used in the polymerization of CN-PDMS-M

		CN-PDMS-M	CN-PDMS$_2$-M	CN-PDMS$_3$-M
D_3	Solution (g)	49.04	49.04	49.04
	D_3 (g)	24.52	24.52	24.52
	mmol	110	110	110
LTMS	Solution (g)	6.40	6.40	6.40
	LTMS (g)	0.48	0.48	0.48
	mmol	5.01	5.01	5.01
Terminating Agent	ID	CP-DMCS	CP-DCMS	CP-TCS
	Mass (g)	0.81	0.46	0.34
	MW (g mol^{-1})	161.71	182.12	202.54
	mmol	5.01	2.51	1.67
Theoretical MW (g mol^{-1})		5,000	10,000	15,000

9.2.4.3. Reduction of nitrile functional groups with sodium borohydride: The reduction of nitrile terminated PMDS macromers with sodium borohydride ($NaBH_4$) was carried out at room temperature with magnetic stirring, in inhibitor-free THF, in

a nitrogen (N_2) glove box for 4 hr. NaBH4 powder was measured into vials in the N_2 glove box. A solution of CN-PDMS-M (50% in THF) was added dropwise to the $NaBH_4$ powder. After the 4 hr reaction time had passed, the reaction mixture was quenched by the dropwise addition of deionized water. Gas (hydrogen) evolved during the quenching stage, and the addition of water was halted when the gas evolution ceased. The reaction mixtures were left stirring overnight at room temperature, in the N_2 glove box. Rotary evaporation and filtration were used to isolate the polymer. Four stoichiometric ratios of CN-PDMS-M were attempted to determine the amount of $NaBH_4$ necessary for reduction of the nitrile functional group to an amine and to determine whether the reducing agent affected the molecular weight of the polymer. The reagents and amounts used in the reduction of nitrile groups on CN-PDMS-M with $NaBH_4$ are shown in Table 9.7. A similar set of reactions was performed under the same conditions, but with a longer reduction time (48 hr). The reagents used for this analysis are outlined in Table 9.8.



Scheme 9.2. Preparation of CN-PDMS-M

Table 9.6. Reagents used in the reduction of nitrile groups on CN-PDMS-M with $LiAlH_4$ for 3 hr

Molar Ratio CN: $LiAlH_4$	Mass $LiAlH_4$ (mg)	CN-PDMS-M Solution (g)	Mass CN-PDMS-M (g)
1:1	3.4	2.5	0.63
1:2	6.8	2.5	0.63
1:5	16.9	2.5	0.63
1:10	33.9	2.5	0.63

Table 9.7. Reagents used in the reduction of nitrile groups on CN-PDMS-M with $NaBH_4$ performed for 4 hr

Molar Ratio CN: $NaBH_4$	Mass $NaBH_4$ (mg)	CN-PDMS-M Solution (g)	Mass CN-PDMS-M (g)
1:1	8	6.0	3.0
1:2	16	6.0	3.0
1:5	41	6.0	3.0
1:10	81	6.0	3.0

Table 9.8 Reagents used in the reduction of nitrile groups on CN-PDMS-M with NaBH4 performed for 48 hr

Sample	Mass $NaBH_4$ (mg)	CN-PDMS-M Solution (g)	Mass CN-PDMS-M (g)
1:1	16	6.0	3.0
1:2	32	6.0	3.0
1:3	48	6.0	3.0
1:4	65	6.0	3.0

9.2.4.4. Symyx® Rapid® GPC: High-throughput gel permeation chromatography (GPC) was used to analyze the molecular weight distributions of the linear and branched PDMS macromers. This analysis was performed relative to polystyrene standards. A polymer concentration of 1-2 mg ml^{-1} in THF and a flow rate of 2.0 mg ml^{-1} were used.

9.2.4.5. NMR spectroscopy: Proton nuclear resonance spectroscopy (^{1}H-NMR) was performed using a Jeol 400 MHz spectrometer fixed with an autosampler. Solutions were prepared at 25 mg ml^{-1} in deuterated chloroform. Sixteen scans were performed with a 0.3 sec delay time.

9.3. Results and discussion

The preparation of branched PDMS macromers was carried out using two synthetic approaches. The challenge of this work was in the preparation of *functional* branched macromers, and controlling the amount of branching that occurred. Allyl ethers were first used in the preparation of branched macromers by hydrosilylation with hydride functional, linear PDMS macromers. However, through hydrosilylation with stoichiometric equivalents, complete hydrosilylation did not occur. Additional allyl ether was added and less control over degree of branching resulted. Another approach was developed to overcome these challenges, where controlled termination of anionic polymerization of PDMS with a series of chlorosilane compounds yielded nitrile functional macromers with varying degrees of branching. The use of the nitrile group was introduced so the functional group could be reduced to a primary amine and used in the preparation of siloxane-polyurethane coatings. However, controlled termination of the polymerization of PDMS and the reduction of the nitrile group also presented challenges in the preparation of branched PDMS macromers.

9.3.1. Branched PDMS macromers from allyl ethers

9.3.1.1. Preparation of branched macromers from allyl ethers (BAE-PDMS-M): The results from the ^{1}H-NMR analysis after hydrosilylation of allyl ethers with

HT-PDMS-M are shown in Figure 9.4. The absence of the silicon-hydride peak can be observed at 4.7 ppm and the presence of small peaks from the residual allyl groups can be observed at 5.2 ppm and 5.8 ppm. The complete reaction of the silicon-hydride peaks was obtained only after the addition of excess allyl ether. When stoichiometric amounts of the functional groups were used, there was always unreacted silicon-hydride. Therefore, after several reaction cycles, additional allyl ether was added, resulting in the spectra shown in Figure 9.4. However, the additional allyl ether that was added resulted in excess allyl functional groups after the reaction of HT-PDMS-M. The allyl ethers were soluble in methanol and the HT-PDMS-M was not, so unreacted allyl ether could be removed by extraction with methanol. For the allyl ethers with multiple allyl groups, it was likely that a distribution of macromers were obtained when excess amounts of these reagents were added. However, the excess allyl ether was added after most of the HT-PDMS-M had reacted to convert the last remaining silicon-hydride functional groups. The intention was that most of the macromers would possess the desired amount of branching.

The results from GPC analysis of the BAE-PDMS-M are shown in Table 9.9. The molecular weight (MW) of HT-PDMS-M was very close to the target MW and the polydispersity (PDI) was the lowest of all of the macromers. The accuracy of the MW with respect to the target MW indicates the success of the anionic polymerization, where the MW was determined by the ratio of initiator to monomer. Furthermore, the PDI of 1.1 indicates that the polymer chains were all very close to

the same MW, as a result of simultaneous initiation and termination of all polymer chains, as is an inherent property of living anionic polymerization.

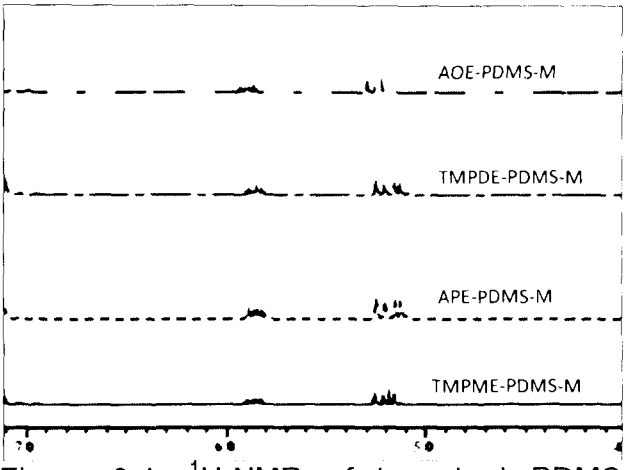


Figure 9.4. ^{1}H-NMR of branched PDMS macromers from allyl ethers

The MW and PDI of TMPME-PDMS-M and AOE-PDMS-M were similar to that of HT-PDMS-M, which was expected since the allyl ethers used to prepare those macromers had single allyl functional groups to react with HT-PDMS-M. The MW distributions of TMPDE-PDMS-M and APE-PDMS-M were slightly different than the others. TMPDE-PDMS-M showed a higher MW and a similar PDI as HT-PDMS-M while APT-PDMS-M showed a higher PDI and similar molecular weight as HT-PDMS-M. The changes in MW were small, and so were the differences in PDI. GPC indirectly measures the MW of polymers by measuring the hydrodynamic volume of a polymer in solution. Therefore, the lack of difference between macromers could have been due to the measurement. The addition of excess allyl ether could have also led to the similarities in MW, where the formation of linear macromers became more likely. Further analysis should have been performed on these samples to better understand the MW distributions of these macromers. For example, analysis by GPC before and after extraction with

methanol may have been helpful in understanding this data, along with other techniques of measuring polymer MW, such as with matrix assisted laser desorption/ionization spectroscopy (MALDI).

Table 9.9 GPC results of branched PDMS macromers from allyl ethers

Sample	$\overline{M_n}$	$\overline{M_w}$	PDI
HT-PDMS-M	5200	5900	1.1
TMPME-PDMS-M	4700	5400	1.2
APE-PDMS-M	4200	6300	1.5
TMPDE-PDMS-M	5400	6600	1.2
AOE-PDMS-M	5300	6500	1.2

9.3.1.2. Siloxane-polyurethane coatings based on BAE-PDMS-M: A series of coatings containing the branched PDMS macromers from allyl ethers were prepared and characterized for contact angle, surface energy, and pseudobarnacle adhesion. The results from water contact angle (WCA) and SE analysis on the siloxane-polyurethane coatings prepared with branched PDMS macromers from allyl ethers are shown in Figure 9.5. The WCA were relatively low compared to siloxane-polyurethane coatings based on aminopropyl terminated PDMS macromers (APT-PDMS-M) which generally show WCA in the range of 100-110°. The WCA of these coatings were in the range of 85-95°. The SE of these coatings were relatively high (30-50 mN/m) compared to coatings prepared with APT-PDMS-M which generally have SE in the range of 22-25 mN/m. Furthermore, the WCA on the siloxane-polyurethane coatings were only about 5-10° higher than for the polyurethane (PU) that did not contain any PDMS. A similar observation was made for SE, where the SE of the coatings containing the PDMS macromers were only slightly reduced, or not reduced at all, compared to the PU coating.

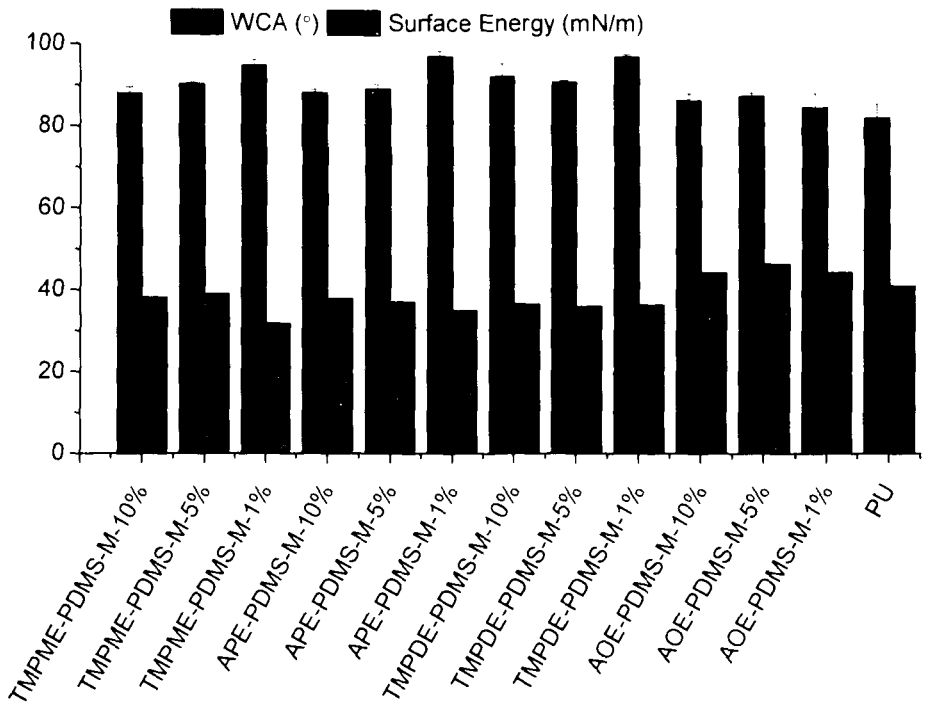


Figure 9.5. Water contact angle (WCA) and SE collected for the siloxane-polyurethane coatings prepared with BAE-PDMS-M where the WCA values are means of three measurements and the error bars represent one standard deviation of the mean. The SE was calculated from mean WCA and methylene iodide contact angle values using the Owens-Wendt method.[16]

During the self-stratification of these coatings, PDMS migrates to the coating surface, and this had been observed for similar coatings in previous chapters. However, in this case, the PDMS was bonded to an allyl ether compound, which was water soluble and hydrophilic as an individual entity. The presence of these groups may have affected the migration of PDMS to the surface of the coatings during film formation by increasing compatibility of the PDMS and the polyurethane bulk which helps drive self-stratification of these coatings. Alternatively, the migration of PDMS to the surface also forces the migration of the hydrophobic allyl ether it was bonded to. This may have caused the formation of a

less hydrophobic surface. The branched structure of the macromers could have also hindered the movement of the PDMS to the coating surface, resulting in a less PDMS at the coating surface. Any of these factors would have influenced the WCA and SE results that were obtained for these systems. Further characterization could be conducted to determine which scenario was more likely.

The results from PB adhesion on the siloxane-polyurethane coatings based on BAE-PDMS-M are shown in Figure 9.6. The PB adhesion was reduced for all of the coatings, compared to the PU control which did not contain PDMS. The coatings which contained APE-PDMS-M and TMPDE-PDMS-M showed the lowest PB removal forces, under 10 N. These macromers were those prepared from allyl ethers with higher levels of allyl functionality, and with higher theoretical levels of branching. Coatings prepared with linear macromers (TMPME-PDMS-M and AOE-PDMS-M) showed the lowest PB removal force when higher levels of PDMS were included in the formulation (10% binder mass). Even though the coatings showed lower WCA and higher SE than expected compared to similar coatings, the PB adhesion of some of the coatings was similar to that observed for coatings prepared in previous chapters, illustrating that this approach to the preparation of siloxane-polyurethane coatings is worth pursuing further, possibly through a different synthetic approach which provides more consistent properties when the macromers are formulated into siloxane-polyurethane fouling-release coatings. Additionally, a different synthetic approach may ensure that the desired level of branching is achieved and that the differences in branching and their effect on coating properties and performance could be better understood.

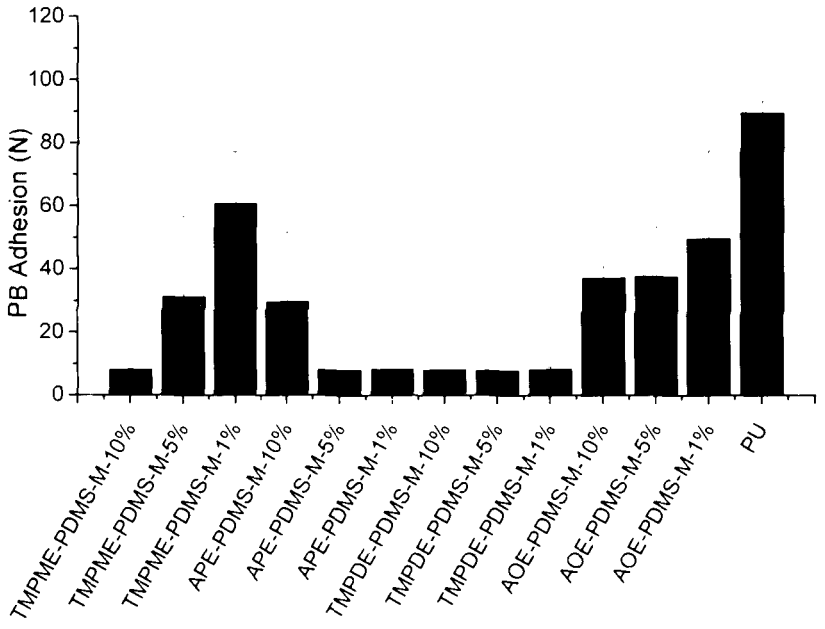


Figure 9.6. PB adhesion on siloxane-polyurethane coatings prepared with BAE-PDMS-M. The values shown are the means of three measurements and the error bars represent one standard deviation of the mean.

9.3.2. Nitrile terminated branched macromers

9.3.2.1. Preparation of nitrile functional branched macromers: The GPC results from the preparation of nitrile functional branched macromers are shown in Table 9.10. CN-PDMS-M showed the lowest molecular weight, and the polydispersity was higher than for previously prepared HT-PDMS-M. This may have been due to the use of the stoichiometric amount of terminating agent, where a 100% molar excess is generally used. This may have led to the presence of living chains in the reaction mixture for longer periods of time where the chains did not encounter terminating species. Additional monomer additions to some polymer chains of chain backbiting as the silanolate chain end remained in the solution may have been caused. Either of these phenomena would have led to chains of varying molecular weight, and a rise in PDI.

The branched macromers (CN-PDMS$_2$-M and CN-PDMS$_3$-M) where multiple PDMS chains were added to a single chain terminator showed higher molecular weight compared to the linear sample (CN-PDMS-M) and higher polydispersity. However, the molecular weight of CN-PDMS$_2$-M and CN-PDMS$_3$-M determined by GPC were similar, suggesting that these macromers occupied the same amount of space in solution. Because CN-PDMS$_3$-M was branched, it may not have occupied more volume in solution and this may have been the cause for the similar GPC molecular weights observed for CN-PDMS$_2$-M and CN-PDMS$_3$-M. Additionally, the PDI of CN-PDMS$_3$-M was higher than for CN-PDMS$_2$-M. This indicates that the polymer chains (or branches) in that sample were not all the same size. Therefore, incomplete branching could have resulted, or uneven monomer additions or backbiting may have been the cause for the high PDI. However, star polymers with similar structures to CN-PDMS$_3$-M have been shown to result in lower molecular weight as stars in GPC than the sum of their linear polymers measured by the same method.[17] To fully understand the cause for the difference, or lack thereof, in molecular weight for these samples, additional characterization could be carried out. Additional experimentation could also be performed to identify the best possible method for the preparation of these macromers and to effectively predict their MW.

Table 9.10. GPC of nitrile functional branched PDMS macromers

Sample	$\overline{M_n}$	$\overline{M_w}$	PDI
CN-PDMS-M	3800	4700	1.2
CN-PDMS$_2$-M	5900	7800	1.3
CN-PDMS$_3$-M	5300	7300	1.4

9.3.2.2. Reduction of nitrile groups in PDMS macromers: The reduction of nitrile terminated PDMS macromers was carried out on CN-PDMS-M, the linear macromer. This was because it was the easiest to prepare, could be prepared with the most predictable outcome, in terms of molecular weight. The objective was to identify an appropriate method for the reduction of the nitrile group on the linear macromer which could be later applied to the branched, nitrile functional PDMS macromers. The first attempt at reduction of the nitrile groups was with $LiAlH_4$, and the GPC results from this reduction are shown in Figure 9.7. As shown, the polymer molecular weight was changed dramatically in the presence of LiAlH4 where greater than a stoichiometric ratio was used. Additionally, there was not a change in peak shifts observed in ^{1}H-NMR, suggesting that the reducing agent likely reacted with the polymer backbone rather than the nitrile functional groups.

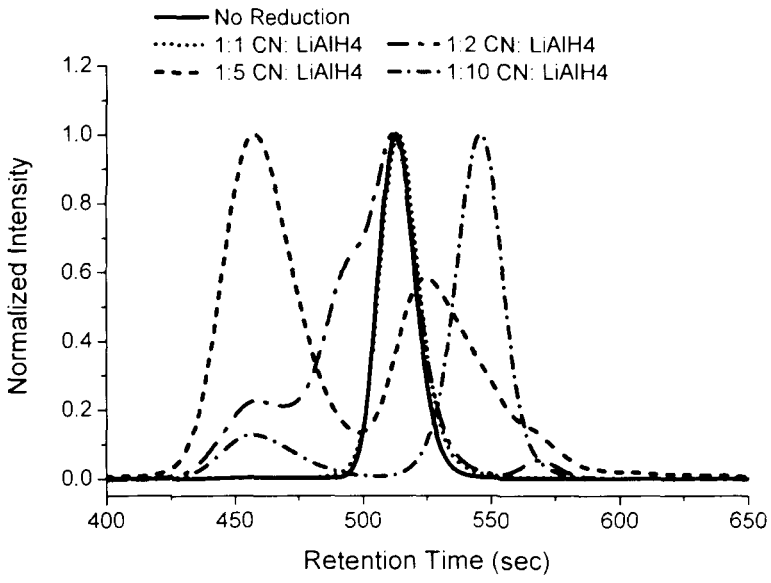


Figure 9.7. GPC traces of CN-PDMS-M reduced with $LiAlH_4$ for 3 hr

Because of the reduced molecular weight and lack of change in the ^{1}H-NMR spectrum upon the attempted nitrile reduction with $LiAlH_4$, this was determined to be an ineffective method for carrying out this reaction. Therefore, the reduction with $NaBH_4$, a different reducing agent which has been reported as non-damaging to the silicon-oxygen bond[18] was attempted. Figure 9.8 and Table 9.11 show the GPC results from the attempted reduction of the nitrile group CN-PDMS-M for 4 hr with $NaBH_4$. While only slight, the molecular weight distribution of the polymer changed during the reaction, and the samples which contained the most $NaBH_4$ showed the greatest change in MW. There was no change observed in the chemical shifts in ^{1}H-NMR, suggesting that the reduction reaction did not occur. Because the 4 hr reaction time resulted in lack of reduction of the nitrile group, an additional series of reactions were carried out where the reduction reaction time was extended to 48 hr. The GPC results from this set of samples are shown in Figure 9.9 and Table 9.12. Again, there was a change in the molecular weight of the macromer, and an increase in the MW was noted. The changes in the MW of the samples were more pronounced than during the 3 hr reaction time. Figure 9.10 shows the ^{1}H-NMR spectra for these samples (which is also representative of other reduction samples) where, again, there was no change observed in the chemical shifts of the peaks representing the macromers. In the sample for which reduction was not attempted, the only difference was additional peaks observed from residual THF, thus confirming the lack of nitrile reduction.

The changes in MW observed during the 48 hr reduction reaction of CN-PDMS-M with $NaBH_4$ were undesired. The reduction reaction is necessary in

functionalizing the polymers for their use in siloxane-polyurethane fouling-release coatings, and this did not occur. The change in molecular weight that occurred during the process defeated the purpose of using living anionic polymerization to prepare the macromers with well-defined molecular weights. It has been reported in literature that dimerization is a common side reaction that occurs in the reduction of nitriles, and this may have been part of the cause for the change (increase) in MW which can be overcome by the addition of acetic anhydride.[19] However, another synthetic approach should be considered for the future of this project. Some work is underway to determine if accelerators can be added to the reduction reaction to increase the reaction rate so that satisfactory reduction of the nitrile group to an amine is obtained with minimal effect on the molecular weight of the macromer. Some of the accelerators that have been reported for reduction using $NaBH_4$ in literature include carboxylic acids, activated charcoal, and cobalt (II) chloride.[20-22]

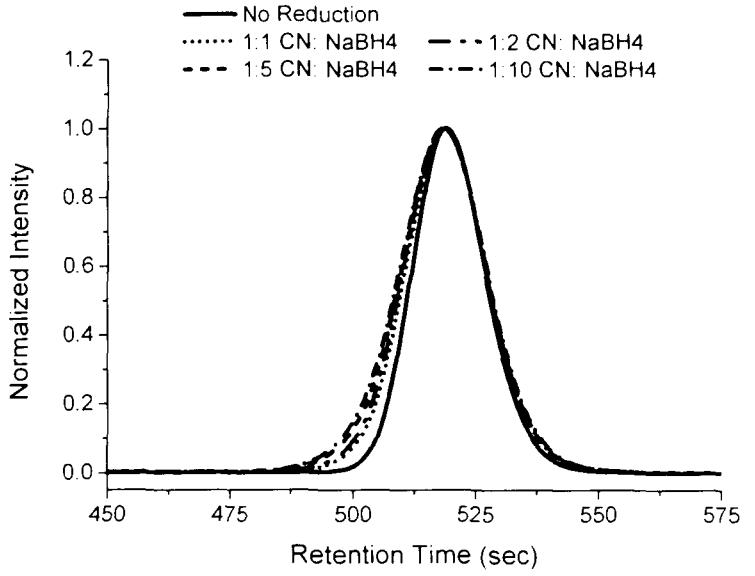


Figure 9.8. GPC results from the 4 hr reduction of CN-PDMS-M with $NaBH_4$

Table 9.11. GPC results from the 4 hr reduction of CN-PDMS-M with $NaBH_4$

Sample	$\overline{M_n}$	$\overline{M_w}$	PDI
No Reduction	6100	6800	1.12
1:1 CN:$NaBH_4$	6200	7200	1.16
1:2 CN:$NaBH_4$	6300	7400	1.18
1:5 CN:$NaBH_4$	6400	7600	1.20
1:10 CN:$NaBH_4$	6400	7700	1.21

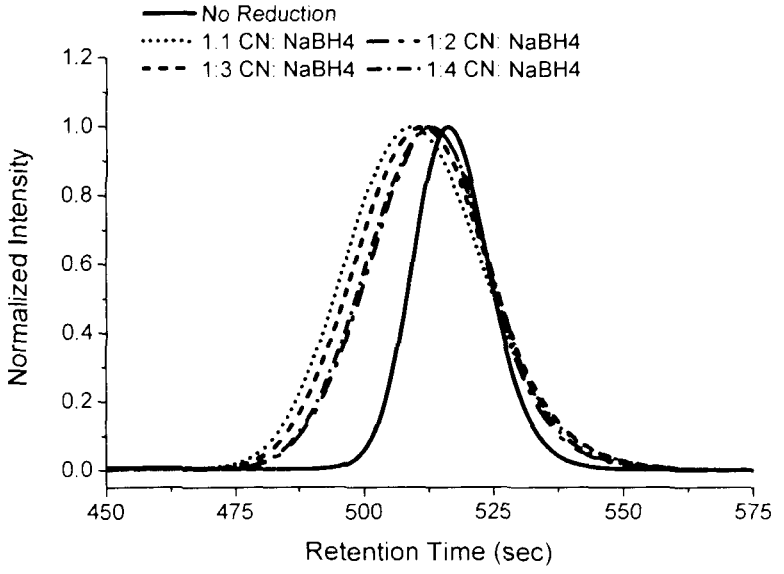


Figure 9.9 GPC results from the 48 hr reduction of CN-PDMS-M with $NaBH_4$

Table 9.12 GPC results from the 48 hr reduction of CN-PDMS-M with $NaBH_4$

Sample ID	$\overline{M_n}$	$\overline{M_w}$	PDI
No Reduction	6900	7700	1.12
1:1 CN:$NaBH_4$	8100	11,500	1.41
1:2 CN:$NaBH_4$	7700	10,100	1.31
1:2 CN:$NaBH_4$	7800	10,800	1.38
1:4 CN:$NaBH_4$	7700	10,200	1.32

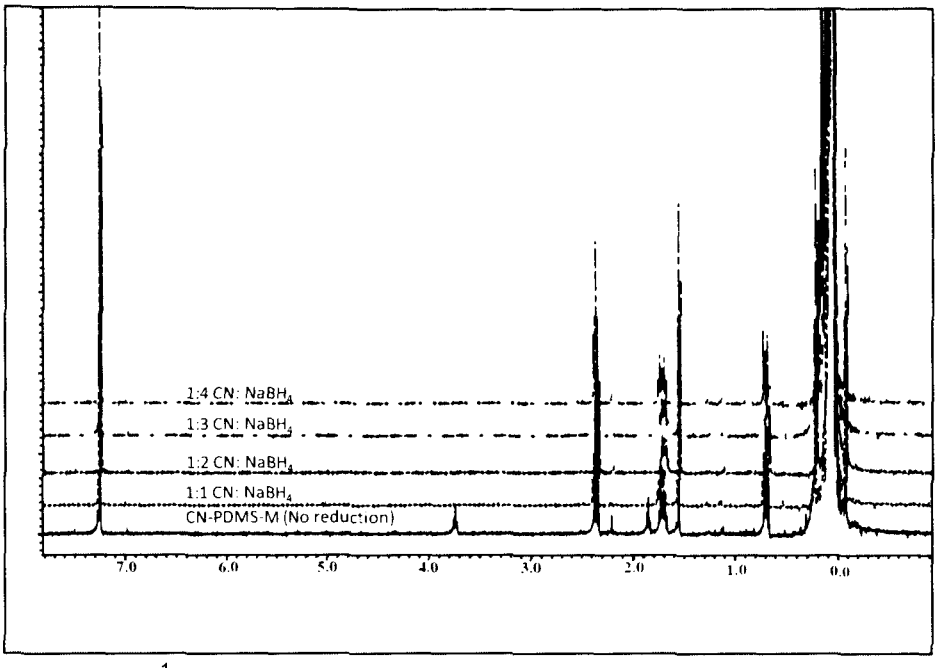


Figure 9.10 ^{1}H-NMR of CN-PDMS-M reduced with $NaBH_4$ for 48 hr

9.4. Summary and conclusions

In this chapter, the preparation of branched PDMS macromers from allyl ethers was shown where the isolation of pure macromers was unlikely due to the addition of excess allyl ether during the hydrosilylation reactions. Siloxane-polyurethane coatings were prepared from these macromers, and found to have only slightly elevated WCA and slightly reduced SE compared to a polyurethane control. However, low PB adhesion was obtained for the coatings which contained the PDMS macromers suspected of having the highest amounts of branching. Therefore, it was determined that branched macromers were worth pursuing in future research, but the development of a more sophisticated synthetic approach was necessary to prepare macromers with the desired amount of branching and that would give the performance desired in siloxane-polyurethane coatings.

The preparation of nitrile functional PDMS macromers followed, where the terminating agent added in the anionic polymerization provided nitrile functionality to the macromers. The nitrile functionality opened another avenue of synthesis where the functional group could be reduced to a primary amine via a standard organic chemistry reduction reaction. However, it was found that common organic reducing agents caused changes in polymer molecular weight, without causing the desired reduction. Therefore, this work is currently incomplete, as methods for accelerating the reduction reaction so that completion is achieved before macromer molecular weight changes occur is being investigated.

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CHAPTER 10. GENERAL CONCLUSIONS AND FUTURE WORK

10.1. Conclusions

The preliminary study on the fouling-release (FR) performance of siloxane-polyurethane coatings based on PDMS macromers illustrated the potential of these coatings to serve as effective FR coatings. The coatings showed low surface energy and pseudobarnacle adhesion, before and after water immersion. In general, the siloxane-polyurethane coatings exhibited performance comparable to fouling release standards, and even commercially available fouling release paints. The general conclusion that PDMS macromers showed promising results and were worth pursuing in future research prompted further exploration of these systems.

In an extended water aging study, the properties and fouling-release performance of siloxane-polyurethane coatings that were water aged for periods of 1, 4, and 8 weeks were studied. Most of the results from this study showed changes in properties when the coatings were exposed to extended water aging cycles. This is undesired, as marine coatings are expected to maintain performance over long periods of time and inconsistency or drop-off in performance and changes in properties could cause major problems for the industry. However, the results that were observed may have been due to an artifact in the experimental method used which resulted in incomplete removal of biomass that was accumulated during aging prior to analysis. Aging in a common tank in the presence of other, possibly less stable coating systems, may have also led to the contamination of the coating surfaces with other organic material. The observations of this and other experiments resulted in the replacement of the water

aging apparatus with a more sophisticated system where sets of similar coatings are aged in individual tanks and the aging water is automatically changed daily. This allows for a researcher to have more faith in results obtained from laboratory biological analysis.

Field testing and underwater hull cleaning experiments demonstrated the potential of siloxane-polyurethane coatings based on PDMS macromers in providing fouling-release performance. In the case of most lab and field tests, the siloxane-polyurethane FR coatings were found to perform comparably to the commercially available fouling-release coatings, IS 700 and IS 900. The siloxane-polyurethane coatings discussed here offer increased durability and adhesion to marine primers while maintaining the fouling-release performance that the currently commercially available fouling-release coatings offer. This was highlighted in the hull cleaning experiments where the elastomeric coatings showed heavy scratching when cleaned with aggressive rotating brush cleaning tools. The siloxane-polyurethane coatings, on the other hand, showed minimal damage. While the most appropriate tools for cleaning elastomeric coatings may be identified as water jets, the siloxane-polyurethane coatings cleaned well with the aggressive brush tools when extremely heavy fouling wasn't present. This would save many hours of work over the lifetime of a ship, even if more frequent cleaning were necessary to prevent the accumulation of severely heavy fouling.

Pigmentation of siloxane-polyurethane coatings was performed to explore the effects on fouling-release performance because commercial paints contain pigment for both cosmetic (i.e. color) and functional purposes (i.e. hiding a

substrate, application, and monitoring of damage). Coatings prepared based on both difunctional PDMS and PDMS macromers showed that any negative effect that pigmentation had on fouling-release performance could be overcome by increasing the PDMS content in the binder of the paint. This was important in the development of these systems and from a commercialization standpoint. If siloxane-polyurethane coatings were to ever be applied to actual marine vessels, the coatings would likely contain pigment. Therefore, it was necessary to understand the effects of pigmentation on the coatings, especially on the self-stratification which drives the polysiloxane to the coating surface and provides release properties. The studies performed showed that the pigmentation of these systems would not interfere with their fouling-release performance.

Finally, the preparation of end-functional homopolymer PDMS brushes and branched PDMS macromers and their incorporation into siloxane-polyurethane coatings shows promise, as several of the systems demonstrated high water contact angle, low surface energy, and low pseudobarnacle removal force. While the preparation of these types of PDMS is more elaborate than linear PDMS macromers and difunctional PDMS, their use in siloxane-polyurethane coatings may prove to enhance overall performance. Furthermore, the more elaborate preparation does not necessarily discredit their use in large volumes of paint, especially if they provide enhanced performance which can reduce the amount of PDMS that needs to be added to achieve the same level of performance. However, the FR performance of coatings based on these types of polymers needs to be assessed to truly understand their utility.

10.2. Future work

The work presented in this dissertation demonstrates the promise of siloxane-polyurethane coatings based on PDMS macromers in providing an effective alternative to traditional silicone-elastomer FR coatings. However, the performance of these coatings in field testing tends to drop-off after approximately six to nine months of immersion. This includes the underwater hull cleaning experiments. The cause for this drop-off in performance is likely due to the accumulation of heavy fouling that occurs as the coatings sit in static immersion sites. It has been suggested that the use of proactive grooming, where regular cleaning of panels is carried out to limit fouling to slimes. During the course of this work, a grooming experiment was set up with collaborators at Florida Institute of Technology where regular cleaning of panels was to occur. Panel corrosion halted this experiment, but the arrangement of another grooming study is underway where the regular cleaning of siloxane-polyurethane coatings will be conducted. This experiment will provide information about the length of time for which heavy fouling can be prevented on these types of coatings, and whether regular cleaning extends the useful lifetime of these types of coatings.

The siloxane-polyurethane coatings prepared in this dissertation and in previous work have involved coatings which are relatively thin compared to traditional FR coatings and the effects of thickness on the performance and properties of siloxane-polyurethane FR coatings has not been explored systematically. With the tools available at NDSU for the rapid screening of coating properties and fouling-release performance via high-throughput laboratory assays,

a systematic study on this property could be carried out fairly easily. Thickness is an important parameter in determining release from traditional silicone elastomer FR coatings and a lot could be learned from a study of the effect of thickness on release from siloxane-polyurethane coatings. For example, there could be a "sweet spot" where the performance of siloxane-polyurethane coatings are optimized and better FR performance could be attained.

Another area of future work is the exploration of the self-stratification that occurs within siloxane-polyurethane coatings and furnishes their FR performance. It would be interesting to explore the factors that affect self-stratification of these coatings and to further characterize their morphology and correlate the results with fouling-release performance. Self-stratification is difficult to understand and to characterize, because it is dependent on many factors within a coating, how it is applied, and the environment it is housed within. Self-stratified coatings are very useful where the marriage of two unique properties is desired, but the process seems only modestly understood and should be explored further. Because siloxane-polyurethane coatings offer so much promise as marine coatings, the fundamental understanding of what drives their success should be better understood.

PDMS macromers have been fairly well studied in their use in siloxane-polyurethane FR coatings in this dissertation. However, their architecture may not be the best route to obtaining the best FR performance. Therefore, the further exploration of advanced and unique polymer architectures and their use in siloxane-polyurethane coatings for marine applications should be further

researched. The development of end-functional PDMS brushes, and the exploration of branch molecular weight, backbone molecular weight, branch density, and polymer functionality should be explored, incorporated into siloxane-polyurethane coatings and tested for FR performance. While current research is ongoing in the assessment of FR performance of these systems, there are many variables than can be explored, such as those mentioned above. The use of combinatorial/high-throughput analysis of these parameters could expedite the experimentation and allow for down-selection where the most promising compositions can be further explored in areas such as marine field testing.

Finally, the preparation of branched PDMS macromers and their incorporation into fouling-release marine coatings has shown promise. However, these species have only begun to be explored. Different synthetic approaches may allow for their easier synthesis and incorporation into siloxane-polyurethane coatings. Once a suitable and reliable synthetic approach has been determined (perhaps through the use of accelerators in the reduction of nitriles to amines), the branching density and branching molecular weight of these systems can be extensively explored to determine their effect on the performance of siloxane-polyurethane fouling-release coatings.