Fouling-Release Performance of Silicone Oil-Modified Siloxane-Polyurethane Coatings

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S *Supporting Information*

ABSTRACT: The effect of incorporation of silicone oils into a siloxane-polyurethane fouling-release coatings system was explored. Incorporation of phenylmethyl silicone oil has been shown to improve the fouling-release performance of silicone-based fouling-release coatings through increased interfacial slippage. The extent of improvement is highly dependent upon the type and composition of silicone oil used. The siloxane-polyurethane (SiPU) coating system is a tough fouling-release solution, which combines the mechanical durability of polyurethane while maintaining comparable fouling-release performance with regard to commercial standards. To further improve the fouling-release performance of the siloxane-PU coating system, the use of phenylmethyl silicones oils was studied. Coatings formulations were prepared incorporating phenylmethyl silicone oils having a range of compositions and viscosities. Contact angle and surface energy measurements were conducted to evaluate the surface wettability of the

Silicone Oil Modified Siloxane-Polyurethane Fouling Release Coating System

coatings. X-ray photoelectron spectroscopy (XPS) depth profiling experiments demonstrated self-stratification of silicone oil along with siloxane to the coating-air interface. Several coating formulations displayed improved or comparable fouling-release performance to commercial standards during laboratory biological assay tests for microalgae (*Navicula incerta*), macroalgae (*Ulva linza*), adult barnacles (*Balanus amphitrite* syn. *Amphibalanus amphitrite*), and mussels (*Geukensia demissa*). Selected silicone-oil-modified siloxane-PU coatings also demonstrated comparable fouling-release performance in field immersion trials. In general, modifying the siloxane-PU fouling-release coatings with a small amount (1−5 wt % basis) of phenylmethyl silicone oil resulted in improved performance in several laboratory biological assays and in long-term field immersion assessments.

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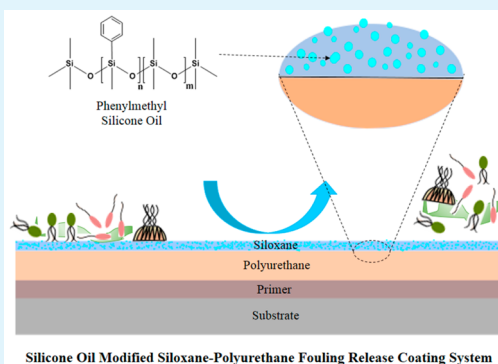
INTRODUCTION

Marine biofouling is the unwanted growth and accumulation of biological organisms on materials submerged in seawater.[1] The process of marine biofouling is a complex phenomenon that can involve more than 4000 marine organisms in multiple stages (Figure 1).[1] Marine biofouling processes begin as soon as a structure is immersed in seawater. First a conditioning film is formed due to the adsorption of organic molecules present in the marine environment. The fouling process is highly dynamic and marine bacteria colonize the surface quickly (min) forming

a bacterial biofilm.[2] Slime forming algae (diatoms) also colonize the surface and contribute to the microfouling community. Macro-foulers such as barnacles and mussels tend to settle within a few days of immersion. However, fouling organisms may settle even without colonization or the presence of other marine organisms.[2,3]
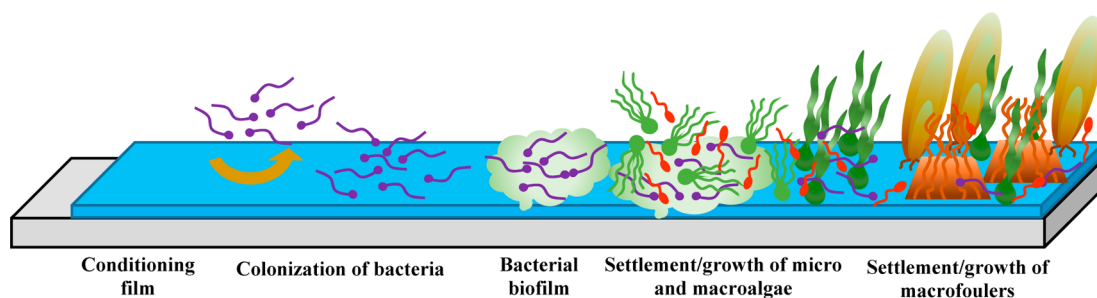
Figure 1. Fouling development on a structure submerged in seawater.

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

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

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

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

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

In this study, silicone oils with a range of phenylmethyl compositions were incorporated into a SiPU coating system at 1, 2, and 5 wt % based on PDMS with the intention of obtaining improved fouling-release performance relative to the first generation SiPU (A4−20) system without oil.[14] Fouling-release performance of these silicone oil-modified coatings was also compared against the commercial fouling-release systems Intersleek700 and Intersleek900. Surface characterization of the experimental coatings was conducted using XPS, contact angle and surface energy measurements. Fouling-release performance of these coatings was evaluated using laboratory biological assays and field immersion studies at multiple test sites.

■ EXPERIMENTAL SECTION

Materials. Phenylmethyl silicone oils (PMM-1025, PMM-1043, PMM-5021, PMM-6025, PMM-0021, and PMM-0025) were purchased from Gelest Inc. Polyisocyanate Desmodur Z 4470 BA was provided by Bayer MaterialScience (now Covestro LLC). Acetylacetone, toluene, methyl amyl ketone (MAK), and dibutyltin diacetate (DBTDAc) were purchased from Sigma-Aldrich. All reagents were used as received. An acrylic polyol containing 80% butyl acrylate

Table 1. Properties of the Phenylmethyl Silicone Oils Used in the Study

name of oil	type	% phenylmethyl	viscosity (cs)	MW (g/mol) reported	surface tension (mN/m)
PMM-1025	copolymer oil	8–12	500	9000–11000	24.4
PMM-1043	copolymer oil	8–12	30000	40000–50000	24.8
PMM-5021	copolymer oil	45–50	125	2000–2200	24.5
PMM-6025	copolymer oil	58–60	500	3500–4000	
PMM-0021	homopolymer oil	100	100–200	700–1200	
PMM-0025	homopolymer oil	100	500	2500–2700	28.5
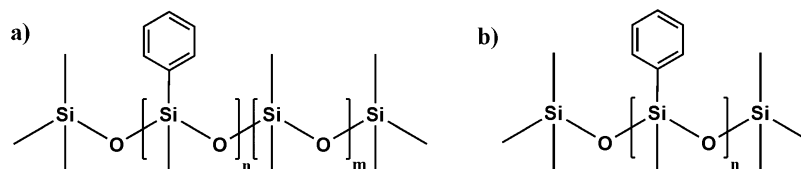
Figure 2. Chemical structure of silicone oils used for the experiment: (a) phenylmethyl dimethylsiloxane copolymer oil and (b) phenylmethyl siloxane homopolymer oil.

(BA) and 20% 2-hydroxyethyl acrylate (HEA) was selected for this study and synthesized as previously reported.[23] An aminopropyl terminated poly(dimethylsiloxane) (APT-PDMS) of 20 000 g/mol molecular weight was synthesized as reported previously.[14] Details of the synthesis of the acrylic polyol and siloxane are provided in the Supporting Information.

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

Table 2. Silicone-Oil-Modified Experimental Coating Compositions

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

Coating Formulation. A general formulation procedure described here was followed. The nonreactive components such as APT-PDMS (20% by wt. based on the total solids of the formulation), corresponding silicone oil (1%, 2%, and 5% based on PDMS wt.), acrylic polyol, and pot life extender were combined in a glass vial and allowed to mix overnight. The next day, 1.1 equiv (for 1 equiv of hydroxyl and amine combined) of isocyanate (Desmodur Z4470 BA) and 0.05% of DBDTAc catalyst were added (using a diluted solution of 1% by wt in MAK). The formulations were allowed to mix for about an hour before coating preparation. Table 2 shows all the experimental coating formulations.

Coating Application and Curing. Drawdowns were made using a wire wound drawdown bar to achieve 80 μm dry film thickness on 8 in. × 4 in. aluminum panels previously primed with Intergard 264

marine grade primer. The coatings were allowed to cure for 24 h under ambient conditions inside a dust free cabinet, followed by forced curing in the oven at 80 °C for 45 min. These panels were used for barnacle and mussel reattachment (1 panel per each test). Coatings for other biological assays (described later) were prepared by depositing 250 μL of formulation in to 24-well plates modified with primed aluminum discs.[24] These were also cured following the same procedure described above.

Control and Standard Coatings. As an internal control, the first generation SiPU formulation (A4-20) was prepared. This is the base coating formulation without the added silicone oil. A pure polyurethane formulation without APT-PDMS was also prepared to be included as a control. Commercial coating standards, Dow Corning T2 (silicone elastomer), Intersleek700 and Intersleek900 (AkzoNobel International Paint), were prepared according to manufacturer's specifications to serve as standards. All internal control coatings and commercial standards were prepared on both primed aluminum panels and in 24-well plates in order to be characterized in parallel with the experimental coatings.

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

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

X-ray photoelectron spectroscopy (XPS) was utilized to investigate the effects of silicone oil incorporation on coating morphology. A Thermo Scientific K-Alpha XPS equipped with monochromatic Al Kα (1486.68 eV) X-ray source and Ar$^+$ ion source (up to 4000 eV) for depth profiling was used for the XPS experiments. Initially an etch rate calibration experiment was performed to determine the appropriate etch rate for depth profiling experiment using thin film of silicone elastomer of known thickness (287.3 nm). Dow Corning T2 silicone elastomer was spin coated on a silicon wafer at a speed of 6000 rpm for 35 s using a Laurell WS-400A-6NPP spin coater. Following spin coating, the sample was carefully transferred to a dust free cabinet and

allowed to cure under ambient conditions. For accurate film thickness measurements, a First Optec Micro Master Excimer laser was used to ablate and remove a thin strip of coating from the spin coated sample and then a KLA-Tencor profilometer was used to measure step height from the top of the coating to the wafer substrate. The thickness of the silicone elastomer was determined to be 287.3 ± 25.3 nm. Depth profiling of the silicone elastomer was performed using a 1000 eV Ar^+ source sputtering on a spot of 1 mm^2 in 30 s intervals for about 50 min (until complete penetration into the silicon wafer). Chamber pressure was maintained below 1.5×10^{-7} Torr. Photoemission lines for C 1s, N 1s, O 1s, and Si 2p were collected after each etch for an interval of 5s at constant analyzer pass energy 155 eV, and an energy increment of 0.167 eV. Silicone elastomer etch rate with Ar^+ ion etch power of 1000 eV was determined to be 0.0384 nm s^{-1}.

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

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

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

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

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

Mussel (Geukensia demissa) Adhesion. The assessment of marine mussel adhesion to the coating surfaces was evaluated using a modified version of previously published protocols.[34−36] Marine ribbed mussels (*Geukensia demissa*; 3−5 cm length) were received from Duke University Marine Laboratory in Beaufort, North Carolina, USA. Prior to the attachment study, a 4 cm long acetal plastic rod (product no. 98873A105, McMaster-Carr) was attached to each mussel perpendicular to the ventral edge, using a 3 M acrylic adhesive (product no. 7467A135, McMaster-Carr). Six mussels were then immobilized on to each coating surface using a custom-designed template fabricated from PVC sheets. The coatings containing immobilized mussels were then placed in an ASW aquarium system and fed daily with live marine phytoplankton (DTs Premium Reef Blend Phytoplankton). The coatings were removed from the ASW aquarium tank system after 3 days of immersion and the total number of mussels exhibiting attachment of byssus threads was recorded for each coating. The plastic rod of each attached mussel was then affixed to individual 5 Newton load cells of a custom-built tensile force gauge where all mussels were pulled off simultaneously (1 mm s^{-1} pull rate). The total force (Newtons) required to completely detach all byssus threads for each mussel was recorded and the mean value of the total number of attached mussels for each coating was calculated.

Field Immersion Study. Select experimental coatings were sent to static ocean immersion field testing sites in Hawaii, California, and Singapore to evaluate their fouling-release performance. Coating formulations 5 and 6 along with controls, A4−20 and Intersleek900

were included in the field study. At each test site, panels were immersed in the ocean about 1 m deep from the water line. Every month, visual inspections were performed before and after water-jet treatments (1.65 or 0.69 MPa).

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

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

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

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

■ RESULTS AND DISCUSSION

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

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

Water and methylene iodide contact angles were measured for the as-made coatings as well as following 28 days of water immersion. Figure 3 b. shows the contact angles of the coatings plotted against the coating compositions. The experimental coating surfaces showed water contact angles (WCA) in the range of 90°−105° suggesting hydrophobic character. Water contact angles for the silicone oil-modified SiPU coatings remained mostly unchanged after 28 days of water immersion.
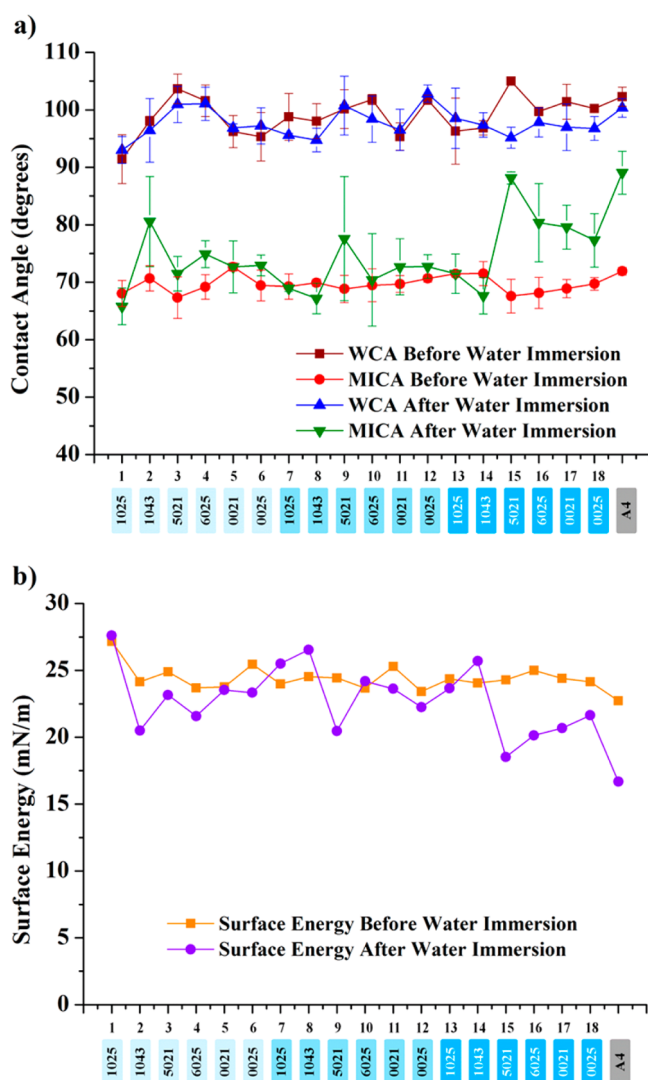

Figure 3. (a) Water and methylene iodide contact angles before and after 28 days of water aging. Each data point represents the average and standard deviation of 3 measurements. (b) Surface energy of coatings calculated by the Owens−Wendt method utilizing the average WCA and MICA measurements. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1−6, 7−12, 13−18), while the darkening of blue shade indicate increasing oil content from 1% and 2% to 5% and the controls and standards are shaded in gray.

The WCA for A4−20 (siloxane-PU without silicone oil) was ∼102°, which is in the same range as silicone oil-modified siloxane-PU coatings signifying self-stratification of siloxane.

Methylene iodide contact angles (MICA) for silicone oil-modified coatings were in the range of 67−71° before water immersion. Although experimental coatings 1−14 did not show much change in MICA after water aging, coatings 15−18 showed an increase in MICA (75−85°) following water aging. Interestingly, the coatings which displayed increased WCA and MICA after water immersion were attributed to formulations modified with phenylmethyl content greater than 50% and oil amount 5%. Figure 3 a. shows the trends in surface energy (SE) changes before and after water immersion. SE values for phenylmethyl silicone oil-modified coatings were very similar to each other prior to water aging. However, after water aging, a slight decrease in SE was observed for silicone oil-modified

coatings 3−6, and 11−13. Coatings 2, 9, and 15−18 showed a significant decrease in SE mainly attributed to the increase in MICA highlighted before. Internal control A4−20 also demonstrated lower surface energy after water immersion. However, in general all coatings surfaces remained hydrophobic after water aging suggesting that no significant surface rearrangement had occurred.

Figure 4a−c shows the atom concentration change determined using XPS of Si, C, O, and N as a function of
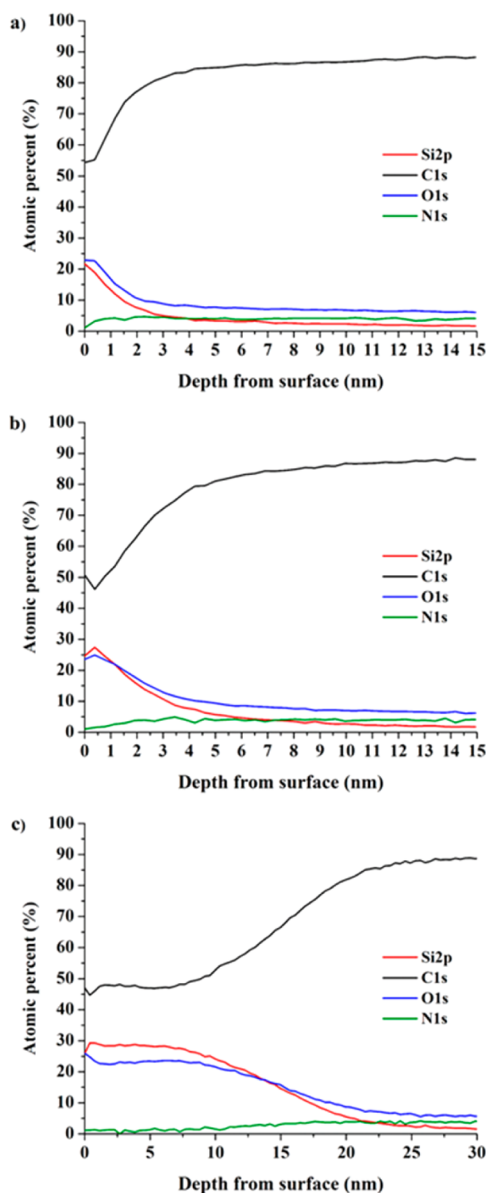
Figure 4. XPS atomic concentration depth profile of (a) A4−20 siloxane-PU without oil, (b) silicone oil-modified formulation 5, and (c) silicone-oil-modified formulation 17.

etch depth from the coating surface (for coatings A4−20, silicone oil-modified formulation 5 and 17). The depth profiling graph (Figure 4 a.) for SiPU without silicone oil (A4−20) showed about 22% surface concentration of Si, which gradually decreased and leveled off to 5% after about 3.5 nm deep into the coating. For the A4−20 coating, the concentration of O followed a similar trend as that for Si, yet slightly higher atomic concentration than Si was observed. The results suggest that

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

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

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

Ulva linza is present in oceans around the world and it is one of the most common species of green macroalgae that contributes to biofouling on ships' hulls.[42] It is known that surface wettability plays a key role in both promoting settlement and adhesion strength of *U. linza*.[43−45] In particular hydrophobic surfaces tend to promote settlement of *U. linza*, whereas spores tend to adhere more strongly to hydrophilic surfaces. Figure 5 shows *U. linza* removal from the experimental, internal control and commercial standard coatings after water-jetting at 9 and 67 kPa. ANOVA's conducted for the *U. linza* removal assay suggest that there are coatings within the set from which removal at both water jet pressures were significantly different (p-value <0.0001, Tables S2 and S5, included in Supporting Information). Several experimental coatings with silicone oil displayed significantly higher sporeling removal compared to all internal control and commercial
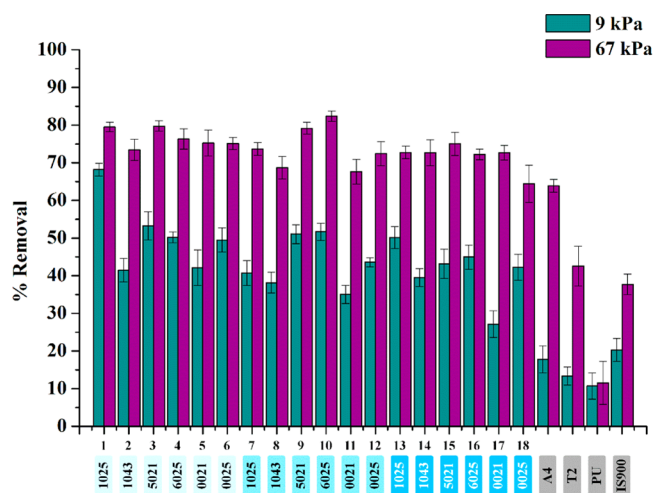
Figure 5. Macroalgae (*Ulva linza*) removal from experimental and control/standard coatings after water-jet treatment at 9 and 67 kPa. Each data point represents the average percent removal value of 6 replicates. Error bars indicate one standard error of the mean. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1−6, 7−12, 13−18) while the darkening of blue shade indicates increasing oil content from 1% and 2% to 5% and the controls and standards are shaded in gray.

standard coatings when subjected to 9 kPa water jet treatment (Figure 5). In particular, a Tukey's comparison test (pairwise comparison) revealed that the phenylmethyl silicone oil-modified coatings, except formulations 11 and 17, showed significantly higher biomass removal compared to A4−20, silicone elastomer (Dow Corning T2), pure polyurethane (PU) and Intersleek 900 (IS 900) (all p-values < 0.05, Table S4). Water-jet treatments conducted at the higher pressure (67 kPa) resulted in more biomass removal from most coatings. Phenylmethyl silicone oil-modified coatings displayed slightly higher removal of sporelings compared to that of A4−20 without silicone oil, yet statistically most experimental coatings were similar in performance against sporeling removal at 67 kPa water-jet pressure (Table S7). However, all silicone oil-modified coatings showed significantly higher sporeling removal when compared to internal controls of T2 and PU and the commercial standard IS 900 (Table S7).

In general, all of the phenylmethyl silicone oil-modified siloxane-PU coatings showed a high removal of sporelings of *U. linza* upon water-jet treatment (Figure 5). Interestingly, silicone-oil-modified experimental coatings demonstrated higher removal of sporelings at low water jet pressures (9k Pa) compared to the internal control A4−20 without any oil, which suggests that incorporation of oil improved sporeling removal from the siloxane-PU system. At water-jet treatments of 9 and 67 kPa, all silicone oil-modified siloxane-PU coatings exceeded the amount of removal observed for the commercial fouling-release coating IS 900 (Figure 5, and Table S4 and S7). Experimental coating formulations 1, 3, 9, and 10 exhibited good fouling-release performance toward sporelings of *U. linza* at both water jet pressures with percent removal values as high as ∼75−80% (Figure 5). These coatings showed statistically higher removal of sporelings of *U. linza* than standard IS 900 and the internal controls, T2 and PU at 95% significance level (all p-values <0.05, Table S3 and S6). Therefore, silicone oil-incorporated coatings seem to impart good fouling-release properties toward *U. linza*. It is apparent that self-segregated

silicone oil may lead to weaker attachment allowing higher biomass removal at low water jet pressure. Greater removal of *U. linza* has been observed with coating surfaces having low SE (ex. PDMS) while removal was extremely poor for those with high SE.[46] It is proposed that the adhesive secreted by the spores spreads more on hydrophilic surfaces covering a greater surface area compared to that on hydrophobic surfaces which leads to easy release when subjected to stress or shear force. The SE of the silicone oil-modified coatings indicates a hydrophobic surface (Figure 3b), thus fouling-release trends for *U. linza* are in agreement with well-accepted studies. Additionally, interfacial slippage introduced by the silicone oil enhanced the easy release of green algae, as fouling-release performance of experimental coatings were significantly superior at very low water-jet pressure (9 kPa) compared to all other coatings. Specifically, silicone oils with 40−60% phenylmethyl content provided the best sporeling release performance at 1−2% oil level (Table S3 and S6).

With respect to the diatom *N. incerta*, the pure polyurethane internal control (PU) and IS 900 standard displayed the highest amount of cell removal (Figure 6,7). Pure polyurethane, which
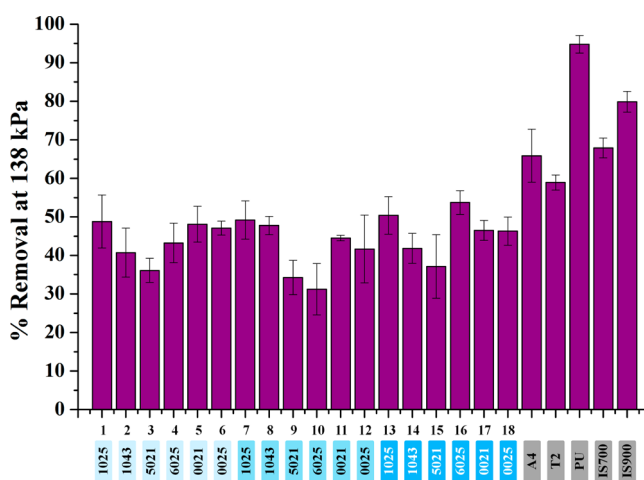
Figure 6. Diatom (*Navicula incerta*) removal from experimental and control/standard coatings after treatments with a 138 kPa (20 psi) water jet pressure for 10 s. Each percent removal value represents the average of 3 replicates samples. Error bars indicate one standard deviation of the mean. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1−6, 7−12, 13−18) while the darkening of blue shade indicates increasing oil content from 1% and 2% to 5% and the controls and standards are shaded in gray.

does not contain any PDMS, exhibited more than 90% *N. incerta* removal. However, all silicone oil-modified coatings displayed impaired removal of *N. incerta* when compared to the A4−20 internal control. The observed results can be explained when one considers the adhesion preference of this diatom strain, which typically adheres more strongly to hydrophobic surfaces than to hydrophilic surfaces (a behavior that is the exact opposite of green algae *U. linza*).[44,47] Contact angle and SE measurements for silicone-oil-modified SiPU coatings indicate hydrophobic surface characteristics (Figure 3a and b). Therefore, diatom removal was negatively affected, which is not unexpected. Coatings which displayed good fouling-release performance toward *U. linza* (1, 3, 9, and 10) performed rather poorly toward *N. incerta* highlighting the complexity of attaining a fouling-release surface which performs well for a
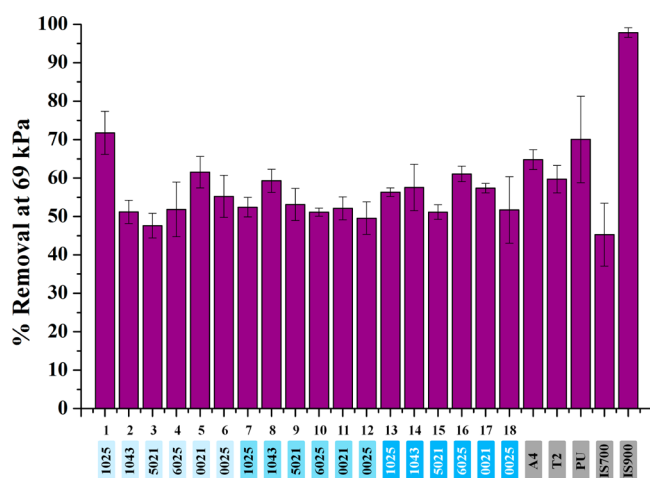
Figure 7. Bacterial (*Cellulophaga lytica*) biofilm removal from experimental and control/standard coatings after being exposed to a 69 kPa (10 psi) water-jet treatment for 5 s. The percent removal values represent the average of 3 replicate samples. Error bars indicate one standard deviation of the mean. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1−6, 7−12, 13−18) while the darkening of blue shade indicates increasing oil content from 1% and 2% to 5% and the controls and standards are shaded in gray.

variety of organisms. The high amount of cell removal observed for IS 900 is attributed to its reported amphiphilic character. The first generation SiPU formulation showed *N. incerta* removal comparable to Intersleek 700 and T2 silicone elastomer. Interestingly, however, the experimental coatings modified with phenylmethyl homopolymer oil (100% phenylmethyl) showed similar *N. incerta* removal at all oil levels (1%, 2%, and 5%).

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

Marine bacterium *Cellulophaga lytica* biofilm removal from coatings after exposure to 69 kPa (10 psi) water jet treatment is shown in Figure 7. Statistical analysis on biofilm removal data for experimental coatings showed that there are formulations with statistically different biofilm removal properties (*p*-value <0.0001, Table S11). The commercial fouling release-coating IS 900 outperformed all of the experimental coatings in terms of biofilm removal (97%), including the five best performing silicone oil-modified coatings (1, 5, 8, 16, and 17) observed in this particular assay (Table S12). However, several siloxane PU-

coatings modified with phenylmethyl silicone oils showed a similar degree of biofilm removal as the IS 700 standard. Coating 1 with 1% of PMM1025 silicone oil showed the greatest removal (72%) of bacterial biofilm out of all the experimental coatings, and at $\alpha = 0.05$ significance level, this formulation also outperformed IS 700 (*p*-value <0.05, Tables S12 and S13). On the other hand, the five best experimental coatings displayed similar bacterial biofilm removal performance to A4−20, Dow Corning T2 and pure polyurethane control coatings (all *p*-values are >0.05, Table S12 and S13). In general, the incorporation of phenylmethyl silicone oil did not affect the bacterial biofilm removal properties of the siloxane-PU system since several experimental coatings showed similar performance to the A4−20 internal control. No significant trend was observed with regard to phenylmethyl composition of silicone oils in this assay.

Macrofouling organisms are the main culprits of heavy calcareous fouling which leads to increased hull roughness and severe powering penalties.[48] Barnacle cyprids are known to conduct surface exploration before permanently cementing themselves (a process known as metamorphism).[49,50] Like other marine organisms, barnacles also display species specific adhesion preferences according to surface chemistry and wettability.[49] Therefore, barnacle adhesion strength to silicone oil-modified coatings reflect the surface properties of these coatings. Figure 8 shows the adhesion strength measurements
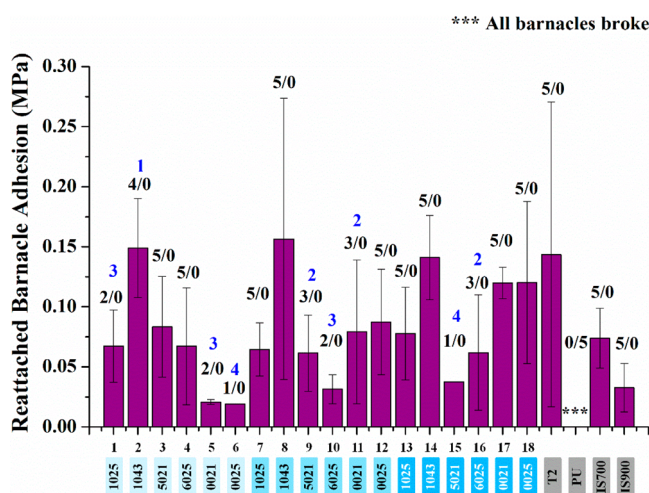
Figure 8. Adhesion of reattached barnacle (*Amphibalanus amphitrite*) experimental and control coatings. Five adult barnacle reattachments were attempted for each coating. Each adhesion strength value represents the average of total number of reattached barnacles released without damage. Error bars represent the standard deviation of average barnacle release stress. The ratio represents the number of measured barnacles over the number of broken/damaged barnacles. The blue digits represent the number of nonattached barnacles. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1−6, 7−12, 13−18) while the darkening of blue shade indicate increasing oil content from 1% and 2% to 5% and the controls and standards are shaded in gray.

of adult barnacles that were reattached to the experimental and control/standard coatings. During this test, reattached barnacles were pushed off in shear using a force gauge. If the barnacle is adhered weakly, the barnacle will release without any damage. Strongly adhered barnacles would break during the test indicating poor fouling-release. For a good fouling-release

coating, the adhesion strength of barnacles should be minimal and have several nonattached barnacles. Poor fouling-release surfaces show high adhesion strength of barnacles and multiple broken barnacles.

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

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

Mussels are fairly large fouling animals which tend to attach to substrate with the use of multiple byssal threads. Several studies have shown that amino acid 3,4-dihydroxyphenyl-L-alanine (DOPA) plays a key role in producing adhesive plaque during mussel attachment to a substrate.[52] Studies have also shown that mussel adhesive plaque spreads the least on low SE surfaces (such as PTFE) and requires more byssal threads to attach to the surface.[52] However, the exact opposite behavior is observed for hydrophilic surfaces. Figure 9 provides the results from the mussel adhesion experiment. Several siloxane-PU coatings had no mussel attachment during the 3-day attachment test. However, a few coatings with phenylmethyl silicone oil displayed minimal mussel attachment where the mussels were released with very low forces. This observation is in agreement with previous findings on the preference of mussel adhesion behavior, where significantly low mussel adhesion strengths were observed for low SE materials. Control coating A4−20 and the IS 900 standard did not enable any mussels to attach to their respective surfaces, which may imply that these coatings perform well against mussel settlement. The viscosity of the silicone oil additive seems to play an important role in the case of mussel adhesion. Interestingly, the experimental coatings which did not enable any mussels to attach contained phenylmethyl silicone oils with similar viscosities, regardless of
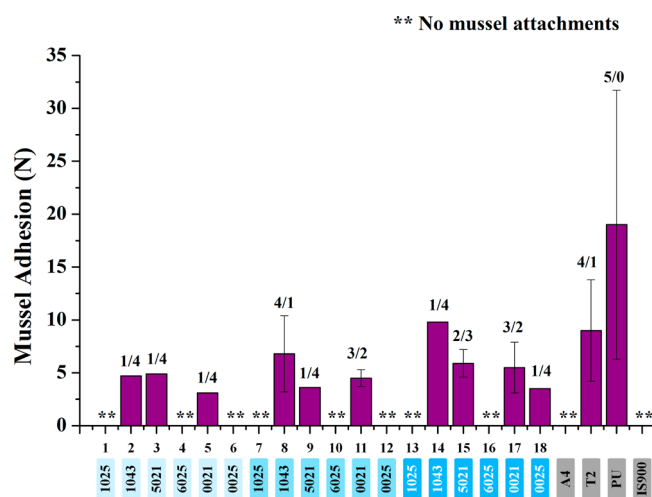
Figure 9. Adhesion of mussels (*Geukensia demissa*) to experimental and control coatings. Five mussels were introduced to each coating. Each adhesion strength value represents the average of total number of attached mussels released from the surface. Error bars represent the standard deviation of the average adhesion force. The ratio represents the number of attached mussels over the number of nonattached mussels. ** indicate the coatings that did not have any attached mussels. Coatings labels: Coatings are arranged in the order of increasing phenylmethyl composition of the silicone oil (ex: 1−6, 7−12, 13−18) while the darkening of blue shade indicates increasing oil content from 1% and 2% to 5% and the controls and standards are shaded in gray.

phenylmethyl composition. It may be hypothesized that the silicone oils with similar viscosity have enough mobility to self-stratify to the surface. Statistical analysis was not performed due to numerous data points with no mussel attachment.

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

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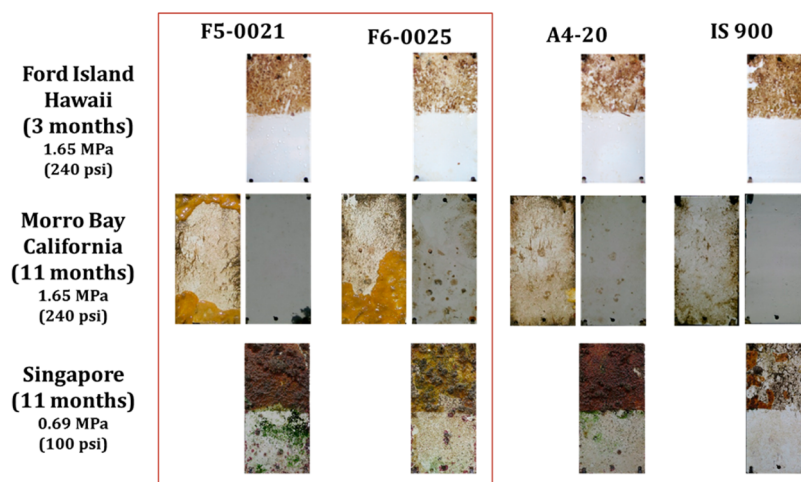
Figure 10. Visual appearance of coatings included in field immersion trials at California, Singapore and Hawaii test sites. In Hawaii and Singapore test sites, half of each panel was subjected to water jet cleaning while the other half represents the accumulated fouling. At the California test site,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

location.[53,54] Although it is well recognized that different seawater parameters such as temperature, salinity, density, and pH have an influence over biofouling, little attention has been given to understand their exact effects.[1]

Incorporation of phenylmethyl silicone oil into siloxane-PU coatings has been shown to improve the fouling-release performance toward macrofouling organisms during laboratory biological assay tests; in particular, for macroalgae sporeling release, where coatings with silicone oils containing <60% phenylmethyl composition showed significantly better performance than the SiPU control and commercial standards. Coatings modified with 1% of silicone oils PMM-0021 and PMM-0025 (phenylmethyl homopolymer) showed reduced barnacle adhesion. For phenylmethyl copolymer oils PMM-5021 and PMM-6025, low barnacle adhesion strength was observed with slightly higher oil amount (2% or 5% by wt.). Several silicone oil-modified coatings showed excellent fouling-release performance toward marine mussels where the SiPU coatings that did not allow any mussels to adhere to their surface contained phenylmethyl silicone oils with a viscosity of 500 cs. However, silicone oil incorporation did not seem to substantially affect the bacterial biofilm and microalgae removal properties compared to the SiPU formulation without silicone oil (A4−20). The field immersion studies showed that incorporating small amounts of phenylmethyl silicone oil could enhance the fouling-release properties of SiPU coatings.

CONCLUSIONS

Previous studies had suggested that inclusion of phenylmethyl silicone oil in silicone elastomer-based fouling-release coatings led to improved fouling-release performance.[15−22] These improvements were reasoned by hypothesizing that the reduced adhesion strength of marine organisms was due to increased interfacial slippage induced by the exuding silicone oil. This study investigated the effects of incorporating phenylmethyl silicone oils in a SiPU fouling-release coating system. Contact angle and surface energy measurements suggested that the coating surfaces were hydrophobic and remained hydrophobic after 1 month of water immersion. XPS analysis was helpful to understand the effects of silicone oil on coating morphology and indicated that stratification of the

silicone oil occurred along with siloxane and formed a thicker interfacial layer. Laboratory biological assays indicated that an improvement in release properties for several types of model fouling organisms might have reflected the silicone oil modification. Siloxane-PU coatings modified with silicone oils demonstrated excellent release properties against the macroalga *U. linza*; high removal was observed at low water-jet pressures. An improvement in lower adhesion strength of macrofouling organisms was also observed with incorporation of silicone oil. In particular, silicone oils with high phenylmethyl composition provided good fouling-release performance toward barnacles (*A. amphitrite*). Excellent fouling-release performance toward marine mussels (*G. demissa*) was observed for coatings containing phenylmethyl silicone oil with an approximate viscosity of 500 cs, regardless of oil type or composition. However, fouling-release performance toward diatoms (*N. incerta*) and bacteria (*C. lytica*) was largely unaffected by silicone oil modification into SiPU coating system. Selected phenylmethyl silicone oil-modified siloxane-PU coatings also displayed long-term fouling-release performance comparable to commercial IS 900 standard during field immersion tests at three different test sites.

ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b09484.

> Film thickness of coatings used for XPS analysis and statistical analysis of the laboratory fouling-release assays (PDF)

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Notes

The authors declare no competing financial interest.

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