Supplemental Information

Comparison of laboratory and field testing performance evaluations of siloxane-polyurethane fouling-release marine coatings

Shane J. Stafslie¹, Stacy Sommer², Dean C. Webster², Rajan Bodkhe², Robert Pieper², Justin Daniels¹, Lyndsi Vander Wal¹, Rhiannon David³, Maureen C. Callow³, James A Callow³, Emily Ralston⁴, Geoff Swain⁴, Lenora Brewer⁵, Dean Wendt⁵, Gary H. Dickinson⁶, Chin-Sing Lim⁶, Serena Lay-Ming Teo⁶

¹North Dakota State University, Center for Nanoscale Science and Engineering

²North Dakota State University, Department of Coatings and Polymeric Materials

³University of Birmingham, School of Biological Sciences

⁴Florida Institute of Technology, Center for Corrosion and Biofouling Control

⁵California Polytechnic State University, Center for Coastal Marine Sciences

⁶National University of Singapore, Department of Biological Sciences

Corresponding author: Dean C. Webster, dean.webster@ndsu.edu

Synthesis of Siloxane-Polyurethane Coatings Systems

Materials

Hexamethylcyclotrisiloxane (D₃), octamethylcyclotetrasiloxane (D₄), bis(3-aminopropyl)-tetramethyldisiloxane (BAPTMDS) and dimethylchlorosilane (DMCS) were purchased from Gelest Inc. Benzyltrimethylammonium hydroxide (40% in methanol), inhibitor-free tetrahydrofuran (THF), acetylacetone (2,4-pentanedione, PD), lithium trimethylsilanolate (LTMS), allylamine, hydroxyethyl 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. 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 FR 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. A control polycaprolactone polyurethane coating system, formulated without PDMS was also included in the analysis.

Synthesis of APT-PDMS

The preparation of this type of polymer has been described previously (Ekin and Webster 2006). The cyclic siloxane monomer, D₄ (50 g), and benzyltrimethylammonium hydroxide solution (0.13

g) were measured into a 250 ml single neck round bottom flask (RBF). Methanol from the catalyst solution was removed using rotary evaporation. The resulting mixture was added to a three neck RBF equipped with an overhead mechanical stirrer, nitrogen inlet, condenser, heating mantle, and temperature controller. BAPTMDs (0.42 g) was added to flask. The reaction mixture was heated to 80 °C for 10 hr with overhead stirring for polymerization. Following polymerization, the cloudy reaction mixture was heated to 170°C for 1 hr to decompose the catalyst, resulting in a clear polymer.

Synthesis of APT-PDMS-M

A similar synthesis of PDMS macromers has been described previously (Sommer et al. 2010). A 50% weight solution of D₃ (260 g) was prepared in inhibitor-free THF (262 g) in a 1000 ml RBF with magnetic stirring at room temperature. Activated molecular sieves (3 g) were added to the solution, and the RBF was sealed with a rubber septum. The solution was degassed by bubbling nitrogen gas (N₂) through it for 1 hr. A nitrogen environment was maintained after degassing. Initiation of the ring opening anionic polymerization was carried out by the addition of LTMS solution (8.5 ml) through the rubber septum using a disposable syringe and needle. The polymerization was allowed to proceed at room temperature for 3 hr with magnetic stirring, in a closed N₂ environment. Termination of the polymerization was carried out by the addition of DMCS (2.5 ml) through the rubber septum using a disposable syringe and needle. Magnetic stirring was continued overnight to allow for termination of all polymer chains. Rotary evaporation was used to remove the THF and excess DMCS. Vacuum filtration allowed for the isolation of monohydride terminated PDMS (HT-PDMS-M) by removing the molecular sieves and lithium chloride precipitate formed during polymerization termination.

To functionalize the PDMS macromer to monoamine terminated PDMS, hydrosilylation of HT-PDMS-M with allylamine was carried out. In a 100 ml RBF fixed with a rubber septum, allylamine (3 g) was mixed with a solution of chloroplatinic acid hexahydrate (0.06 g) in inhibitor-free THF (18 g). The resulting solution was heated to 60°C for 1 hr with a venting needle placed through the rubber septum. After heating, the mixture was added to a 500 ml RBF with HT-PDMS-M (225 g). The RBF was sealed with a rubber septum and the reaction mixture was degassed by bubbling N₂ through it for 15 min. A venting needle was added to the RBF through the rubber septum, and the reaction mixture was heated at 90°C for 24 hr. The completion of reaction was determined by the absence of the silicone hydride peak at 4.7 ppm in proton nuclear magnetic resonance spectroscopy (¹H-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.

High-throughput 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. The results are shown in Table S1.

Table S1. 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
D-PDMS	30,000	31,800	54,100	1.7
M-PDMS	30,000	28,400	31,800	1.1

Preparation of acrylic polyol

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 to the flask 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 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.

Siloxane-polyurethane coating formulation

The siloxane-polyurethane coating formulations were prepared in two different ways, depending on the type of PDMS included in the formulation. The amounts of each component used in the formulation of the siloxane-polyurethane coatings are also outlined in Table S2. The formulations prepared with m-PDMS (PCL-M10, PCL-M20, ACR-M10, ACR-M20) were prepared by pre-mixing the PDMS 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 formulations prepared with d-PDMS (PCL-D10, PCL-D20, ACR-D10, ACR-D20) were prepared by mixing the PDMS and polyol solution overnight. The following day, PD, IDT, and DBTDAc solution were added, with mixing between additions. All formulations were mixed by magnetic stirring for 1 hr prior to coating application.

Preparation of siloxane-polyurethane and standard coatings

The siloxane-polyurethane coatings were prepared in 24-well plates on aluminum disks and on aluminum Q-panels (10.16 x 20.32 cm (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 μ m primer thickness) via air-assisted spray application. In 24-well plates, 250 μ l was deposited into each well, and coverage of the entire primed aluminum disk was ensured by gentle agitation of the plate. 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 FR performance of the siloxane-polyurethane coatings in the laboratory were compared to commercial FR standards from International Paint (Intersleek®700 (IS 700) and Intersleek®900 (IS 900)), a silicone standard (Silastic T2 (T2)), and a polyurethane control prepared without PDMS. For the IS 700 and IS 900, 0.x ml of tie coat was deposited and cured prior to the addition of 0.x ml of top coat. For T2 and PU controls, 0.25 ml of coating solution was deposited into each well.

Performance evaluations in the field were compared to IS 700, IS 900 and BRA 640, a commercial copper ablative coating manufactured by International Paint. The coatings were prepared according to the manufacturer's specifications and applied via drawdown to the primed aluminum panels using the drawdown procedure described above.

Table S2. Components and amounts used in the formulation of siloxane-polyurethane coatings.

Coating ID	PDMS		Tolonate IDT 70B	Polyol Solution			DBTDA Solution	PD
	Type	(g)	(g)	Polyol Type	Solids/Solvent	(g)	(g)	(g)
PCL-M10	M	13.0	113.2	PCL	90% in MAK	42.0	1.3	16.9
PCL-M20	M	26.0	100.7	PCL	90% in MAK	37.3	1.3	16.5
PCL-D10	D	13.0	113.2	PCL	90% in MAK	41.9	1.3	16.9
PCL-D20	D	26.0	100.8	PCL	90% in MAK	37.1	1.3	16.5
ACR-M10	M	10.0	50.6	ACR	50% in Toluene	109.1	1.0	17.1
ACR-M20	M	20.0	45.1	ACR	50% in Toluene	96.8	1.0	16.3
ACR-D10	D	10.0	50.7	ACR	50% in Toluene	109.0	1.0	17.1
ACR-D20	D	20.0	45.4	ACR	50% in Toluene	96.5	1.0	16.3

M = monofunctional, D = difunctional, PCL = polycaprolactone, ACR = acrylic

Characterization of siloxane-polyurethane coatings

Surface energy and water contact angle

SE analysis was performed on a Symyx® Coatings Surface Energy System with First Ten Ångströms™ software. The contact angles of three droplets of water and three droplets of MI 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 (Owens and Wendt 1969).

Pseudobarnacle adhesion

The removal forces required to remove epoxy-glued studs (PBs) from the surface of the coatings were measured using a Symyx® Automated Pull-Off Adhesion station (Chisholm et al. 2007). 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.

Laboratory assessment of fouling-release performance

Materials

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 (*C. lytica*) or 0.5g of dextrose (*H. pacifica*) per 1L of ASW. Algal growth medium (F/2) consisted of 1L of ASW supplemented with nutrients to generate Guillard's F/2 medium (Guillard and Ryther 1962; Holland et al. 2004). 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).

Water immersion preconditioning

Prior to FR performance assessments in the laboratory, the coatings were immersed in an automated water preconditioning tank system to facilitate the leaching/removal of any potential toxic impurities (i.e., residual solvent, monomers, catalyst) that may have been present in the cured coating films. The tank system was supplied with a continuous flow of tap water at a rate of 7.57 liters/hr. Every four hours (six times/day), the water in each tank was removed by vacuum/suction and passed through particulate and activated carbon filters to remove any coating degradation products and dissolved organics. This process also served to enhance the rate of leaching of the coatings prepared in the multi-well plate format by actively exchanging the entire volume of water in each well. Upon completion of the water immersion preconditioning process, the surface of the coatings were mechanically cleaned with a polyurethane foam pad and then allowed to dry under ambient conditions. The coatings prepared for bacteria, diatom and barnacle analysis were immersed for four weeks while the coatings prepared for the *Ulva* sporelings assay were immersed for two weeks prior to analysis.

Toxicity assessments of coating leachates

Toxicity assessments of coating leachates were performed after water immersion preconditioning to ensure that all potentially toxic impurities had been removed from the cured coating films prior to conducting FR performance evaluations. The specifics of the methods used to assess the toxicity of coating leachates towards the suite of fouling organisms employed in this study have been reported in detail in a recent publication by the authors (Webster and Bodkhe 2015).

Bacterial biofilm retraction and removal

The analysis of *C. lytica* biofilm retraction was performed on the coatings deposited in 24-well plates as previously described (Stafslien et al. 2007a; Stafslie et al. 2006). Briefly, the coatings were inoculated with 1.0 ml of a suspension of *C. lytica* in BGM (10^7 cells ml⁻¹) and the plates were incubated for 24 hr at 28°C under static conditions. 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 and subsequently stained with crystal violet (0.3% w/v in deionized water) for 15 min. The plates were rinsed three times with ASW to remove excess crystal violet, tapped firmly on an absorbent pad and allowed to dry at ambient laboratory conditions. The degree of biofilm retraction on each coating surface (i.e., percent surface coverage) was then quantified using a customized automated image-based software program as described in detail in a previous publication by the authors (Ribeiro et al. 2008).

Bacterial biofilm removal was carried out by exposing retained biofilms to a pressurized stream of ASW using an automated water jet apparatus (Stafslien et al. 2007b). The coatings were inoculated with 1.0 ml of a BGM suspension of *C. lytica* or *H. pacifica* at $\sim 10^5$ cells ml⁻¹ and incubated statically for 24 hr at 28°C. The plates were then transferred to the deck of an automated water-jet apparatus. Three replicate wells, for each coating composition, were excluded from water-jet

treatments and were used to measure the initial amount of biofilm retained on each coating surface. The remaining replicate wells were treated with the water-jet apparatus at an 81 kPa (*C. lytica*) or 111 kPa (*H. pacifica*) impact pressure for 5 s. After water-jet treatments, the plates were stained with 0.5 mL of crystal violet, rinsed three times with ASW water and allowed to dry at ambient laboratory conditions for 1 hr. Digital images were captured of each plate and 0.5 mL of 33% acetic acid was then added to each well for 15 min to solubilize the crystal violet dye retained in the adherent biofilm on the coating surfaces. 0.15 mL of the eluate from each well was transferred to a 96-well plate and measured for absorbance at 600 nm using a multi-well plate spectrophotometer. The percent removal was recorded as the difference in absorbance values between the coating replicates that were exposed to the water-jet and those which were not.

Microalgae cell attachment and removal

The characterization of microalgae cell attachment and removal on coatings prepared in 24-well plates has been described previously (Casse et al. 2007). Briefly, the coatings were inoculated with 1.0 ml of *N. incerta* suspension in F/2 (0.03 OD₆₆₀ or $\sim 10^5$ cells ml⁻¹) and incubated statically for 2 hr at room temperature to facilitate cell attachment. The plates were then transferred to the deck of an automated water-jet apparatus and three replicates of each coating were water jetted at 81 kPa for 10 sec. Three replicates wells of each coating were left untreated and served as initial cell attachment measurements. To each well, 0.5 ml of DMSO was added and the plates were incubated statically in the dark for 20 min to extract chlorophyll *a*. The resulting eluates were transferred (0.15 ml) to a 96-well plate and fluorescence measurements were acquired 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 untreated wells and those treated with the water jet.

Ulva sporeling removal

The *Ulva* sporeling removal assay has been previously described (Callow et al. 1997). Coatings were equilibrated in deionized water for 48 hr and subsequently in ASW for 2 hr prior to analysis. *Ulva* spores were released 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 $\mu\text{mol m}^{-2} \text{s}^{-1}$) and the nutrients were renewed every 48 hr. Following the growth period, six replicate wells were exposed to 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.

Adult barnacle reattachment

The FR performance of the coatings with regards to shell fouling was assessed with an adult barnacle reattachment assay, as previously described (Rittschof et al. 2008; Stafslie et al. 2012). Nine adult barnacles (*Amphibalanus amphitrite* = (*Balanus amphitrite*)) of a testable size (>5mm basal diameter) were dislodged from glass panels coated with a silicone elastomer (Silastic-T2 on glass) and placed on the surface of the coatings produced for the study. Immobilization templates were applied to each panel and then transferred to an artificial salt water aquarium tank system. The reattached barnacles were fed daily with freshly hatched brine shrimp nauplii (*Artemia* sp.). After 14 days of reattachment in the aquarium system, the coatings were removed and the barnacles were dislodged with a hand-held force gauge in shear to measure the peak force at release. Once the force gauge measurements were completed, the area of the barnacle base plates were measured using a Sigma Scan Pro 5.0 software package and the adhesion strengths were calculated by dividing the force required to remove the barnacles by the basal area. Barnacle adhesion for each coating was reported as the mean value of the total number of barnacles that had a measurable detachment force. Barnacles that had no measurable force for detachment were counted as “not attached” and not included in adhesion calculations.

Static Ocean Immersion - California Polytechnic University (Cal Poly)

Four replicates of each coating system were immersed at the Cal Poly test site on May 29th, 2009, 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 0.6 – 1.0 meters (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, anemones, 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 encrusting bryozoan *Watersipora subtorquata*.

Adhesion of fouling organisms was measured using a water jet (Swain and Schultz 1996b; Swain et al. 1997). 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). Note that the tank pressure is directly correlated to the water jet force on the surface of the coating panel (Swain and Schultz 1996b). The water stream was applied perpendicular to and approximately 2.5 cm 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.

The method used for measuring barnacle adhesion is based on ASTM D 5618-94. A shear force was applied to the base of the barnacle using a hand held force gauge, at the rate of approximately 4.5 N s^{-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) is then 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.

Static Ocean Immersion - 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.

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. (Swain and Schultz 1996a) Initial pressure was set to 50 psi. A patch (approximately 2.5 by 4 cm (1" by 1.5")) 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.

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.

Static Ocean Immersion – National University of Singapore (NUS)

Four replicates of each coating system were immersed at the NUS test site located on the west coast of Singapore (1°17' 39.22"N, 103°45'35.4"E) on May 30th, 2009. The Singapore test site is characterized by tropical sea temperatures with monsoon-driven seasonality pattern. Located in an estuary within the Port of Singapore, the site experiences high nutrient levels and rich organism biodiversity. 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. 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.

Table S3. Spearman's rank correlation coefficient (r_s) p -values for the laboratory screening assays.

Laboratory Assay	Laboratory Assay						
	PB Adhesion	<i>C. lytica</i> Removal	<i>C. lytica</i> Retraction	<i>H. pacifica</i> Removal	<i>N. incerta</i> Removal	<i>Ulva</i> Removal	Barnacle Adhesion
PB Adhesion	*****	0.2931	0.0778	0.8810	<i>0.0075</i>	0.0873	0.6515
<i>C. lytica</i> Removal	0.2931	*****	<i>0.0009</i>	0.8810	<i>0.0376</i>	<i>0.0017</i>	0.2291
<i>C. lytica</i> Retraction	0.0778	<i>0.0009</i>	*****	0.7437	<i>0.0113</i>	<i>0.0004</i>	0.0563
<i>H. pacifica</i> Removal	0.8810	0.8810	0.7437	*****	0.5334	0.8277	0.8028
<i>N. incerta</i> Removal	<i>0.0075</i>	<i>0.0376</i>	<i>0.0113</i>	0.5334	*****	<i>0.0104</i>	0.4888
<i>Ulva</i> Removal	0.0873	<i>0.0017</i>	<i>0.0004</i>	0.8277	<i>0.0104</i>	*****	0.1839
Barnacle Adhesion	0.6515	0.2291	0.0563	0.8028	0.4888	0.1839	*****

Bold and italicized values indicate significant model ($\alpha = 0.05$).

Table S4. Spearman's rank correlation coefficient (r_s) p -values for the field testing assessments.

Field Test	Field Test											
	CP Slime 1	CP Slime 3	CP Slime 6	CP Soft 1	CP Soft 3	CP Soft 6	CP Hard 1	CP Hard 3	CP Hard 6	CP Barn	FIT Slime	FIT Barn
CP Slime 1	*****	0.871 5	0.078 1	0.001 6	0.001 9	0.305 7	0.0059	0.1041	0.0348	0.002 4	0.016 8	0.179 3
CP Slime 3	0.871 5	*****	0.648 0	0.540 3	0.889 1	0.035 8	0.3972	0.3384	0.2016	0.629 0	0.425 1	0.138 3
CP Slime 6	0.078 1	0.648 0	*****	0.141 5	0.097 3	0.229 6	0.0443	0.0389	0.0164	0.079 6	0.216 6	0.179 3
CP Soft 1	0.001 6	0.540 3	0.141 5	*****	0.002 4	0.028 8	0.0002	0.0069	0.0041	0.061 1	0.037 6	0.060 8
CP Soft 3	0.001 9	0.889 1	0.097 3	0.002 4	*****	0.203 7	0.0098	0.0232	0.0099	0.007 4	0.032 1	0.063 0
CP Soft 6	0.305 7	0.035 8	0.229 6	0.028 8	0.203 7	*****	0.0033	0.0025	0.0039	0.374 4	0.445 3	0.106 7
CP Hard 1	0.005 9	0.397 2	0.044 3	0.000 2	0.009 8	0.003 3	*****	0.0004	<0.000 1	0.017 2	0.025 7	0.113 1
CP Hard 3	0.104 1	0.338 4	0.038 9	0.006 9	0.023 2	0.002 5	0.0004	****	<0.000 1	0.099 1	0.057 9	0.203 2
CP Hard 6	0.034 8	0.201 6	0.016 4	0.004 1	0.009 9	0.003 9	<0.000 1	<0.000 1	*****	0.038 0	0.044 5	0.088 9
CP Barn	0.002 4	0.629 0	0.079 6	0.061 1	0.007 4	0.374 4	0.0172	0.0991	0.0380	*****	0.006 1	0.295 3
FIT Slime	0.016 8	0.425 1	0.216 6	0.037 6	0.032 1	0.445 3	0.0257	0.0579	0.0445	0.006 1	*****	0.326 3
FIT Barn	0.179 3	0.138 3	0.179 3	0.060 8	0.063 0	0.106 7	0.1131	0.2032	0.0889	0.295 3	0.326 3	*****

Bold and italicized values indicate significant model ($\alpha = 0.05$).

Table S5. Spearman’s rank correlation coefficient (r_s) p -values for the comparisons between laboratory assays and field testing assessments.

Laboratory Assay	Field Test											
	CP Slime 1	CP Slime 3	CP Slime 6	CP Soft 1	CP Soft 3	CP Soft 6	CP Hard 1	CP Hard 3	CP Hard 6	CP Barn	FIT Slime	FIT Barn
PB Adhesion	0.1735	0.2633	0.3241	0.3332	0.3179	0.8694	0.3127	0.4082	0.3419	0.1210	0.0031	0.8535
<i>C. lytica</i> Removal	0.0145	0.5182	0.6648	0.0155	0.0011	0.4382	0.0645	0.1452	0.1512	0.0211	0.0302	0.0904
<i>C. lytica</i> Retraction	0.0138	0.8557	0.3500	0.0007	0.0029	0.1461	0.0077	0.0169	0.0250	0.0493	0.0039	0.0805
<i>H. pacifica</i> Removal	0.9574	0.3608	0.2312	0.6493	0.6263	0.5325	0.7933	0.4620	0.4846	0.6505	0.7228	0.3802
<i>N. incerta</i> Removal	0.0109	0.4310	0.6510	0.0408	0.1061	0.7731	0.1069	0.4401	0.3056	0.0590	0.0051	0.3056
<i>Ulva</i> Removal	0.0035	0.3723	0.2116	0.0037	0.0054	0.4035	0.0251	0.0825	0.1083	0.0309	0.0143	0.3972
Barnacle Adhesion	0.0764	0.2028	0.0624	0.0063	0.0306	0.0046	0.0009	0.0001	<0.0001	0.1315	0.1025	0.2098

Bold and italicized values indicate significant model ($\alpha = 0.05$).

Supplementary Figure:

Figure S1. Biofilm retraction (A) and water jet removal (B) of *C. lytica*, and water jet removal of *H. pacifica* (C) where the bacteria have been stained with crystal violet and the purple color indicates the presence of bacterial biofilm.

Color-coded Tables

Table 3. Spearman's rank correlation coefficients (r_s) for laboratory screening assays.

Laboratory Assay	Laboratory Assay						
	PB Adhesion	<i>C. lytica</i> Removal	<i>C. lytica</i> Retraction	<i>H. pacifica</i> Removal	<i>N. incerta</i> Removal	<i>Ulva</i> Removal	Barnacle Adhesion
PB Adhesion	*****	0.37	0.58	0.06	0.78*	0.57	0.16
<i>C. lytica</i> Removal	0.37	*****	0.88*	0.06	0.66*	0.85*	0.42
<i>C. lytica</i> Retraction	0.58	0.88*	*****	-0.12	0.76*	0.90*	0.62
<i>H. pacifica</i> Removal	0.06	0.06	-0.12	*****	0.22	-0.08	-0.09
<i>N. incerta</i> Removal	0.78*	0.66*	0.76*	0.22	*****	0.76*	0.25
<i>Ulva</i> Removal	0.57	0.85*	0.90*	-0.08	0.76*	*****	0.45
Barnacle Adhesion	0.16	0.42	0.62	-0.09	0.25	0.45	*****

Barn = barnacle, PB = pseudobarnacle. Green, yellow, orange and red shading indicates high ($|r_s| = 0.70-1.0$), moderate ($|r_s| = 0.50-0.69$), low ($|r_s| = 0.30-0.49$) and no ($|r_s| = 0.00-0.29$) correlation, respectively. *Statistically significant model ($\alpha = 0.05$).

Table 5. Spearman's rank correlation coefficients (r_s) for field testing assessments.

Field Test	Field Test											
	CP Slime 1	CP Slime 3	CP Slime 6	CP Soft 1	CP Soft 3	CP Soft 6	CP Hard 1	CP Hard 3	CP Hard 6	CP Barn	FIT Slime	FIT Barn
CP Slime 1	-----	-0.06	-0.58	0.86*	0.85*	0.36	0.80*	0.54	0.67*	0.84*	0.73*	0.46
CP Slime 3	-0.06	-----	-0.17	0.22	0.05	0.67*	0.30	0.34	0.44	-0.17	-0.28	0.50
CP Slime 6	-0.58	-0.17	-----	-0.50	-0.55	-0.42	-0.65*	-0.66*	-0.73*	-0.58	-0.43	0.46
CP Soft 1	0.86*	0.22	-0.50	-----	0.84*	0.69*	0.91*	0.79*	0.82*	0.61	0.66*	0.61
CP Soft 3	0.85*	0.05	-0.55	0.84*	-----	0.44	0.77*	0.70*	0.77*	0.78*	0.68*	0.61
CP Soft 6	0.36	0.67*	-0.42	0.69*	0.44	-----	0.83*	0.84*	0.82*	0.32	0.27	0.54
CP Hard 1	0.80*	0.30	-0.65*	0.91*	0.77*	0.83*	-----	0.90*	0.93*	0.73*	0.70*	0.53
CP Hard 3	0.54	0.34	-0.66*	0.79*	0.70*	0.84*	0.90*	-----	0.95*	0.55	0.62	0.44
CP Hard 6	0.67*	0.44	-0.73*	0.82*	0.77*	0.82*	0.93*	0.95*	-----	0.66*	0.64*	0.56
CP Barn	0.84*	-0.17	-0.58	0.61	0.78*	0.32	0.73*	0.55	0.66*	-----	0.79*	0.37
FIT Slime	0.73*	-0.28	-0.43	0.66*	0.68*	0.27	0.70*	0.62	0.64*	0.79*	-----	0.35
FIT Barn	0.46	0.50	0.46	0.61	0.61	0.54	0.53	0.44	0.56	0.37	0.35	-----

CP = Cal Poly, FIT = Florida Institute of Technology, 1 = one month immersion, 3 = three months immersion, 6 = six months immersion, Barn = barnacle. Green, yellow, orange and red shading indicates high ($|r_s| = 0.70-1.0$), moderate ($|r_s| = 0.50-0.69$), low ($|r_s| = 0.30-0.49$) and no ($|r_s| = 0.00-0.29$) correlation, respectively. *Statistically significant model ($\alpha = 0.05$).

Table 6. Spearman's rank correlation coefficients (r_s) for comparisons between individual laboratory assays and individual field assessments.

Laboratory Assay	Field Test											
	CP Slime 1	CP Slime 3	CP Slime 6	CP Soft 1	CP Soft 3	CP Soft 6	CP Hard 1	CP Hard 3	CP Hard 6	CP Barn	FIT Slime	FIT Barn
PB Adhesion	0.47	-0.39	-0.35	0.34	0.35	-0.06	0.36	0.29	0.34	0.52	0.83*	0.07
<i>C. lytica</i> Removal	0.74*	-0.23	-0.16	0.73*	0.87*	0.28	0.60	0.50	0.49	0.71*	0.68*	0.56
<i>C. lytica</i> Retraction	0.74*	-0.07	-0.33	0.88*	0.83*	0.49	0.78*	0.73*	0.70*	0.63*	0.82*	0.58
<i>H. pacifica</i> Removal	0.02	-0.32	0.42	-0.16	-0.18	-0.22	-0.10	-0.26	-0.25	0.16	0.13	-0.31
<i>N. incerta</i> Removal	0.76*	-0.28	-0.16	0.65*	0.54	0.10	0.54	0.28	0.36	0.61	0.80*	0.36
<i>Ulva</i> Removal	0.82*	-0.32	-0.43	0.82*	0.80*	0.30	0.70*	0.57	0.54	0.68*	0.74*	0.30
Barnacle Adhesion	0.58	0.44	-0.61	0.79*	0.68*	0.81*	0.88*	0.93*	0.93*	0.51	0.55	0.43

CP = Cal-Poly, FIT = Florida Institute of Technology, 1 = one month immersion, 3 = three months immersion, 6 = six months immersion, Barn = barnacle, PB = pseudobarnacle. Green, yellow, orange and red shading indicates high ($|r_s| = 0.70-1.0$), moderate ($|r_s| = 0.50-0.69$), low ($|r_s| = 0.30-0.49$) and no ($|r_s| = 0.00-0.29$) correlation, respectively. *Statistically significant model ($\alpha = 0.05$).

Table 7. Spearman's rank correlation coefficients (r_s) and p values for comparisons between individual laboratory assay rankings and average field assessment rankings.

Laboratory Assay	r_s	p value
PB Adhesion	0.30	0.4047
<i>C. lytica</i> Removal	0.62	0.0537
<i>C. lytica</i> Retraction	*0.77	0.0093
<i>H. pacifica</i> Removal	0.21	0.5563
<i>N. incerta</i> Removal	0.52	0.1276
<i>Ulva</i> Removal	0.59	0.0717
Barnacle Adhesion	*0.83	0.0029

Barn = barnacle, PB = pseudobarnacle. Green, yellow, orange and red shading indicates high ($|r_s| = 0.70-1.0$), moderate ($|r_s| = 0.50-0.69$), low ($|r_s| = 0.30-0.49$) and no ($|r_s| = 0.00-0.29$) correlation, respectively. *Statistically significant model ($\alpha = 0.05$).

References

- Callow ME, Callow JA, Pickett-Heaps JD, and Wetherbee R. 1997. Primary adhesion of *Enteromorpha* (Chlorophyta, Ulvales) propagules: quantitative settlement studies and video microscopy. *J Phycolgy* 33:938-947.
- Casse F, Stafslie SJ, Bahr JA, Daniels J, Finlay JA, Callow JA, and Callow ME. 2007. Combinatorial materials research applied to the development of new surface coatings V. Application of a spinning water-jet for the semi-high throughput assessment of the attachment strength of marine fouling algae. *Biofouling* 23(1/2):121-130.
- Chisholm BJ, Webster DC, Bennett JC, Berry M, Christianson D, Kim J, Mayo B, and Gubbins N. 2007. Combinatorial materials research applied to the development of new surface coatings VII: An automated system for adhesion testing. *Rev Sci Instrum* 78(7):072213.
- Ekin A, and Webster DC. 2006. Library synthesis and characterization of 3-aminopropyl-terminated poly(dimethylsiloxane)s and poly(ϵ -caprolactone)-b-poly(dimethylsiloxane)s. *J Polym Sci Part A: Polym Chem* 44:4880-4894.
- Guillard RRL, and Ryther JH. 1962. Studies of marine planktonic diatoms. I. *Cyclotella nana* hustedt, and *Detonula confervacea* (cleve) gran. *Can J Microbiol* 8(2):229-239.
- Holland R, Dugdale TM, R RW, Brennan AB, Finlay JA, Callow JA, and Callow ME. 2004. Adhesion and Motility of Fouling Diatoms on a Silicone Elastomer. *Biofouling* 20:323-329.
- Owens DK, and Wendt RC. 1969. Estimation of the surface free energy of polymers. *J Appl Polym Sci* 13(8):1741 - 1747.
- Ribeiro E, Stafslie SJ, Casse F, Callow JA, Callow ME, Pieper RJ, Daniels JW, Bahr JA, and Webster DC. 2008. Automated Image-Based Method for Laboratory Screening of Coating Libraries for Adhesion of Algae and Bacterial Biofilms. *Journal of Combinatorial Chemistry* 10(4):586-594.
- Rittschof D, Orihuela B, Stafslie S, Daniels J, Christianson D, Chisholm B, and Holm E. 2008. Barnacle reattachment: a tool for studying barnacle adhesion. *Biofouling* 24(1):1-9.
- Sommer S, Ekin A, Webster D, Stafslie S, Daniels J, VanderWal L, Thompson S, Callow M, and Callow J. 2010. A preliminary study on the properties and fouling-release performance of siloxane-polyurethane coatings prepared from poly(dimethylsiloxane) (PDMS) macromers. *Biofouling* 26(8):961-972.
- Stafslie S, Daniels J, Bahr J, Chisholm B, Ekin A, Webster D, Orihuela B, and Rittschof D. 2012. An improved laboratory reattachment method for the rapid assessment of adult barnacle adhesion strength to fouling-release marine coatings. *J Coat Technol Res* 9(6):651-665.
- Stafslie S, Daniels J, Mayo B, Christianson DA, Chisholm B, Ekin A, Webster DC, and Swain GW. 2007a. Combinatorial Materials Research Applied to the Development of New Surface Coatings. IV: A high-throughput bacterial retention and retraction assay for screening fouling-release performance of coatings. *Biofouling* 23(1):45-54.
- Stafslie SJ, Bahr JA, Daniels JW, Vander Wal L, Nevins J, Smith J, Schiele K, and Chisholm B. 2007b. Combinatorial materials research applied to the development of new surface coatings VI: An automated spinning water jet apparatus for the high-throughput characterization of fouling-release marine coatings. *Rev Sci Instrum* 78(7):072204/072201-072204/072206.
- Stafslie SJ, Bahr JA, Feser JM, Weisz JC, Chisholm BJ, Ready TE, and Boudjouk P. 2006. Combinatorial Materials Research Applied to the Development of New Surface Coatings I: A Multiwell Plate Screening Method for the High-Throughput Assessment of Bacterial Biofilm Retention on Surfaces. *Journal of Combinatorial Chemistry* 8(2):156-162.
- Swain GW, and Schultz MP. 1996a. The testing and evaluation of non-toxic antifouling coatings. *Biofouling: The Journal of Bioadhesion and Biofilm Research* 10(1):187 - 197.

- Swain GW, and Schultz MP. 1996b. The testing and evaluation of nontoxic antifouling coatings. *Biofouling* 10(1-3):187-197.
- Swain GWJ, Schultz MP, Griffith JR, and Snyder S. 1997. The Relationship Between Barnacle and Pseudo-barnacle Adhesion Measurements: A Method to Predict the Foul Release Properties of Silicones? US Pacific Rim Workshop on "Emerging Nonmetallic Materials for the Marine Environment. Honolulu, Hawaii: Office of Naval Research. p paper 10.
- Webster DC, and Bodkhe R. 2015. Functionalized silicones with polyalkylene oxide side chains.