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

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Abstract

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

Key Words

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

Introduction

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

Contending with biofouling has been a challenging problem since the beginning of navigation.² Extensive and rapid buildup of fouling on a ship hull causes reduction in ship speed and maneuverability which in turn increases operating costs and environmental penalties.^{6 7 8} Environmental concerns include the spreading of non-native species around the world and increased emissions due to decreased fuel efficiency. It is estimated that marine biofouling costs the United States Navy approximately 56 million dollars per year (for their mid-sized vessels) and it could add up to 1 billion dollars for 15 years.^{7 8} Historically, copper and lead sheathing covering the ship hulls were used as the primary method of controlling biofouling.² Advancements in polymer and resin technology in the 1960 - 1970s led to the use of self-polishing copolymers with

controlled release of biocides such as tributyl tin (TBT).^{1 2} However, by the late 1970s the deleterious effects of TBT towards non-targeted aquatic life was recognized. This issue was addressed by introducing new regulations to reduce the use of TBT which later culminated in a complete ban of tin based antifouling paints by the International Maritime Organization (IMO) in 2003.¹ Antifouling technologies using copper oxide (CuO) as biocides have predominated in recent decades.⁹ More recently, a considerable amount of research has been conducted towards using non-toxic anti-fouling (AF)/fouling release (FR) technologies that are environmentally friendly.³

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

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

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

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

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

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

Experimental

Materials

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

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

Synthesis of pre-polymers

A commercially available IPDI trimer (Desmodur Z4470 BA) polyisocyanate was modified with PDMS and polyethylene glycol to prepare pre-polymers with several different compositions (Table 1). A general formulation procedure for pre-polymer IPDI-10-5kPDMS-550PEG (formulation 8) modified with PDMS (MW=5000) and PEG (MW=550) is described here (for the pre-polymer described here, amount of PDMS and PEG are 10% each by wt. based on the total weight of final SiPU formulation). First PEG (1.6000g) was diluted with EEP (1.6000g) in a 40 mL glass vial with

a magnetic stir bar. Next, PDMS (1.6000g) was added to the vial and mixed using a vortex mixer for 5 mins. Isocyanate (2.4567g) and DBTDAc catalyst solution (1% by wt. in MAK) (0.3200g) were added into the vial. The contents were mixed using a vortex mixer for 5-10 min followed by further stirring for 24 hrs using a magnetic stir bar. The isocyanate to total hydroxyl equivalents ratio was maintained at 3:2 for all pre-polymers. Detailed formulations can be found in Supplemental Information Table S1.

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

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

Isocyanate titrations

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

Instrumentation

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

Coating Formulation and Curing

Formulation of coatings containing the pre-polymers described before is provided here. Coating formulation was carried out as follows: additional polyisocyanate (5.5314g), acrylic polyol (14.4166g, BA: HEA 80:20 in 50% toluene) and pot life extender acetylacetone (0.3200g) were added into the vial containing the pre-polymer. The overall isocyanate to total hydroxyl equivalents was maintained at 1.1:1 for the final formulation. The contents were thoroughly mixed using a vortex mixer followed by magnetic stirring for 1 hr. Coating formulations were deposited into multi-well plates and drawdowns were prepared on primed aluminum panels. Coating formulations (250 μ L) were deposited using an automatic repeat pipette to each well in multi-well plates. Drawdowns were made using a wire-wound drawdown bar with a wet film thickness of 80 μ m on 8"×4" primed aluminum panels. All coatings were allowed to cure under ambient conditions for 24 hrs followed

by oven curing at 80 °C for 45 mins. All other consequent formulations were also prepared following a similar procedure. In this study, PDMS and PEG levels of 5% and 10% were considered based on the overall coating formulation. Table 1 summarizes the compositional details of 12 experimental coating included in this study.

Table 1: Coating compositions

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

Control and Standard Coatings

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

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

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

Water Aging

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

Biological Laboratory Assays

Growth and Release of Macroalgae (*Ulva linza*)

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

to each well followed by determining fluorescence at excitation at 360 nm and emission at 670 nm wavelengths. Fluorescence is directly proportional to the biomass present on each coating surface. The removal of sporelings at each pressure was compared with the unsprayed wells (that were used to assess sporeling growth above).

Growth and Release of Microalgae (*Navicula incerta*)

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

Bacterial (*Cellulophaga lytica*) Biofilm Adhesion

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

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

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

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

Mussel (*Geukensia demissa*) Adhesion

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

Surface Characterization

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

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

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

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

Results and Discussion

Opposing preferences for surface wettability by marine organisms makes it challenging to formulate anti-fouling/fouling release (FR) coatings that have good performance towards a broad spectrum of organisms. Therefore, the amphiphilic strategy appears to be a viable approach to

combat biofouling. However achieving a suitable hydrophobic vs. hydrophilic balance is challenging. This study investigated the FR performance of AmSiPU coatings formulation containing a hydrophobic component of PDMS and hydrophilic component of PEG. During this study, a series of isophorone diisocyanate (IPDI) based pre-polymers modified with PDMS and PEG were synthesized. These pre-polymers were used to prepare amphiphilic siloxane polyurethane FR coatings (AmSiPU). IPDI trimer (Desmodur Z4470 BA) was reacted with polyethyleneglycol methyl ether (PEG) and a monocarbinol terminated polydimethyl siloxane (PDMS) at different equivalent ratios to obtain pre-polymers with compositional variation. PDMS with three different molecular weights (1000, 5000 and 10000 g/mol) and PEG with two molecular weight variations (550, 750 g/mol) were used for pre-polymer synthesis.

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

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

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

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

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

During the coating formulation step, the isocyanate pre-polymers were mixed with acrylic polyol and additional IPDI trimer (Desmodur Z4470 BA) so that the final content of PDMS and PEG would be either 5 or 10 % by wt on a resin solids basis. This way the compositional variations in isocyanate pre-polymers were translated into the coating formulations. Surface characteristics and morphology of the experimental coatings were studied using contact angle measurements,

ATR-FTIR, XPS, and AFM. Coatings obtained from this experiment displayed amphiphilic character indicating the presence of both hydrophobic PDMS and hydrophilic PEG moieties on the coatings' surfaces.

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

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

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

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

ATR-FTIR provides information about chemical functional groups present on the top surface of solid materials. The penetration depth of ATR-FTIR varies from 0.5 to 2 μ m depending on the angle of incidence, wavelength of light and the refractive indices of ATR crystal and the material of interest. Figure 5 shows the ATR-FTIR spectra for coatings 7, 8 and 9 (Table 1). These coatings had 10% PDMS and PEG content (based on the total solids) with PEG 550 being used in all three. Data for PDMS molecular weights 1000, 5000 to 10000 are provided. The FTIR spectra show the presence of -C-O-C- (1180 cm^{-1}) and -Si-O-Si- (1020-1100 cm^{-1}) functionalities suggesting the presence of both PEG and PDMS. However -Si-O-Si- (1020-1100 cm^{-1}) and Si-CH₃ (790 cm^{-1}) peaks were less prominent in coatings 8 and 9 compared to coating 7. In addition, the peaks corresponding to PEG were slightly lower in intensity for coating 7 compared to the

other two coatings. Therefore, coating 7 had a significant amount of siloxane closer to the surface compared to the other two coatings. The spectra showed the presence of two types of carbonyl groups $C=O''$ (1750 cm^{-1}) and $C=O^*$ (1690 cm^{-1}). The $C=O''$ corresponds to the carbonyl on the acrylic polyol and the $C=O^*$ corresponds to the carbamate group. The peak for $R-CO-NH-R'$ was weak but visible at $3350\text{-}3450\text{ cm}^{-1}$ suggesting a very low concentration closer to the coating surface.

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

XPS spectra of AmSiPU coatings 10, 11 and 12 were obtained to analyze the surface chemical compositions and to observe changes due to variation in PEG and PDMS components. Spectra were obtained at an angle normal (90°) to the surface. Photoemission lines for C 1s, O 1s, N 1s and Si 2p were observed for each sample. Curve fitting was performed based on the possible chemical composition of AmSiPU formulations. Table 4 shows the estimates of atom % based on

peak fitting for each coating and Figure 6 shows the spectra for C 1s and O 1s for totals and the fit. Si 2p peak at around 101.87 eV is indicative of siloxane.³⁸ A small amount of nitrogen from urethane links was also present on the surface as indicated by N 1s peak at 400.08 eV.³⁹ However, the C 1s peak was indicative of several chemical states as there was C from several functional groups (carbonyl, ester, ether and carbon attached to N in isocyanate). Therefore, C 1s peak was fitted with three distinctive sub peaks for C=O at 288.89 eV (from urethane and acrylate groups), C-C-O/C-C-N at 286.19 eV (from ether, and carbon next to isocyanate nitrogen), and all other C-C/C-H at 284.45 eV.⁴⁰ Similarly O 1s was fitted with corresponding peaks for C=O at 533.7 eV (from urethane and acrylate groups), C-O-C at 531.48 eV (ether from PEG) and Si-O-Si at 532.05 eV (from siloxane).

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

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

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

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

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

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

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

All biological laboratory assays were conducted following 28 days of water immersion and assessments of leachate toxicity (using *C.lytica* and *N.incerta*) as described previously.⁴¹ Briefly, overnight extracts of the coatings were collected and inoculated with algae and bacterial. Growth of algae was quantified by fluorescence of chlorophyll after 48 hrs and growth of bacteria was quantified via crystal violet absorbance. Fluorescence and absorbance measurements of the coating extracts were then compared to positive and negative growth controls. Leachates from all

experimental coatings did not show toxicity (data not reported), thus biological laboratory assays were carried out to evaluate their fouling release properties.

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

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

The diatom (*N.incerta*) is a known slime forming microalgae. Fouling-release performance towards *N. incerta* was evaluated using a water-jetting assay. *N.incerta* has been shown to possess a higher affinity towards hydrophobic surfaces compared to hydrophilic surfaces.^{44 46} In terms of cell attachment, most AmSiPU coatings displayed similar biomass compared to control coatings with the exception of Hempasil® X3 silicone hydrogel FR coating. Many AmSiPU coatings with 10% concentration of PDMS and PEG had a slightly lower amount of initial diatom cell attachment. Coating compositions 7, 10 and 11 showed the highest removal of diatoms after 20 psi water-jet treatment which was similar to the performance of Intersleek 1100® SR, Intersleek® 900, polyurethane, and Hempasil® X3 standard coatings. The same AmSiPU

coatings also have $\approx 65\%$ FR performance compared to the 1st generation SiPU coating (A4-20).¹⁴ Coatings consisting of pre-polymer modified with 10% PEG 550 or PEG 750 showed the best FR performance towards the diatoms, suggesting that the amount of PEG may have an important role in affecting diatom adhesion strength. It is also important to point out that several AmSiPU coatings were on par with amphiphilic FR commercial standards considering their FR performance towards microalgae.

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

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

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

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

Macrofouling organisms such as barnacles and mussels, can cause a significant reduction in operational efficiency of marine vessels. Barnacle adhesion strength towards coatings was evaluated using a two week reattachment assay followed by a push off test. Adhesion strength (or critical removal stress) was quantified by shear force for removal divided by barnacle basal plate area. The effects of PDMS MW was clearly seen by the barnacle adhesion strength for AmSiPU coatings (Figure 12). Coatings containing pre-polymers modified with shorter PDMS chains showed high barnacle adhesion strength. The opposite behavior was observed for coatings modified with longer PDMS chains (10000). Also the coatings with higher PDMS MW had no broken barnacles, which is further evidence that PDMS MW had a significant effect on easy release of barnacles attached to surfaces. Several experimental coatings showed non-attached barnacles and lower adhesion strengths that were comparable to Intersleek® 900 performance. Coatings 3, 6, 9, 11, and 12 displayed the best performance allowing removal of all reattached barnacles with lower adhesion strengths. On these coatings, several barnacles were unable to re-attach; further indicator of good FR performance. Coatings consisting of pre-polymer with 10% concentration of PDMS and PEG provided the better FR performance towards barnacles compared to those with 5%. Surface wettability and surface charge play an important role in barnacle settlement.⁴⁷ It is often observed that PDMS based materials show low critical removal stress of barnacles (*A.amphitrite*) which is attributed to their low surface energy.⁴⁷ However AmSiPU coatings with both hydrophilic PEG and hydrophobic PDMS displayed lower barnacle adhesion strengths. This assay demonstrates the important role of PDMS being an essential component in amphiphilic fouling release system. Compared to previous attempts of

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

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

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

In general, coating compositions 7, 9, 10, 11, and 12 exhibited broad-spectrum FR properties towards macroalgae (*U.linza*), bacteria (*C.lytica*), diatom (*N.incerta*), barnacle (*A.amphitrite*) and mussel (*G.demissa*) and were comparable to or exceeded the performance of the commercially available FR standards such as Intersleek 900, 1100SR and Hempasil X3. Coatings comprising both 10% PDMS and PEG were more efficient at promoting the release of these organisms when compared to coatings based on 5% PDMS and PEG. Also PEG 750 showed enhanced FR properties towards microfouling as compared to PEG 550. Macrofouling release efficiency depended primarily upon the composition of PDMS, where macrofoulers were easily released

from coatings containing the high PDMS MW. Surface characterization techniques demonstrated that both hydrophobic and hydrophilic moieties were present on the surfaces of the AmSiPU coatings. However, the surface morphology was clearly affected by the pre-polymer chemical compositional variations. Differences in surface morphology might also explain the improvement in fouling release performance of certain coatings compared to others. As SiPU coatings rely on self-stratification for fouling release properties, there are more variables that need to be considered for fine tuning surface properties of these AmSiPU which need to be addressed in future.

Conclusions

Several pre-polymers with compositional variation in PDMS and PEG were synthesized and incorporated into a siloxane polyurethane (SiPU) coating system. Coatings derived from these novel pre-polymers demonstrated amphiphilic surface properties. Surface wettability of the coatings remained mostly unchanged before and after water aging. Self-stratification of PDMS and PEG moieties was evident from ATR-FTIR, XPS and AFM characterization. ATR-FTIR suggests that both PDMS and PEG are present on the surface after water aging. Surface morphology of AmSiPU coatings were clearly affected by the variations in PDMS and PEG components used for pre-polymer synthesis. XPS spectra indicated that increasing PDMS MW in pre-polymers resulted in higher self-segregation of siloxane increasing the concentration of hydrophobic moieties. AFM images of AmSiPU coatings showed the presence of microdomains with soft and hard segments indicative of phase separation on the surface. Several coatings showed excellent FR performance towards bacteria (*C.lytica*), in terms of water jet removal of attached sporelings. In most cases, >90% of bacterial biofilms were cleaned off after a 20 psi water jet treatment. Fouling release performance of AmSiPU coatings also showed significant improvement in microalgae (*N.incerta*) compared to internal control A4-20 (1st generation SiPU). Interestingly, many of the AmSiPU coatings demonstrated comparable or superior fouling release

properties towards bacteria and microalgae in comparison to the state-of-the-art commercial fouling release coatings. Biological assays for macroalgae (*U.linza*), suggest that AmSiPU coatings have similar fouling release performance compared to Intersleek 1100SR despite the inclusion of hydrophilic PEG. The adhesion strength of barnacles was very low and some non-attached barnacles were observed for several AmSiPU coatings. Generally most AmSiPU coatings displayed similar fouling release properties to Intersleek® 900 in relation to barnacle attachment. Marine mussel (*G.demissa*) adhesion was observed for coatings which performed well in microfouling release. However, the mussels were easily removed with a low force. In general, coatings comprised of pre-polymer with 10% of PDMS and PEG perform better than the ones derived from 5% PDMS and PEG. Also coatings made using PEG MW of 750 showed better FR properties in many assays when compared to the ones with PEG 550; which implies that longer PEG chain may be more effective in FR. A number of coatings provided broad-spectrum FR properties for a variety of representative marine organisms with diverse adhesion profiles, suggesting amphiphilic coatings are very effective in combating biofouling. Overall AmSiPU coatings showed superior or comparable FR properties to the leading commercial standards such as Intersleek® 900, Intersleek® 1100SR and Hempasil® X3 but with the additional desirable features of being tougher and more durable.

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

References

- 1 Yebra, DM, Kiil, SK and Dam-Johansen, K, "Antifouling technology—past, present and future steps towards efficient and environmentally friendly antifouling coatings." *Progress in Organic Coatings*, 50 (2) 75-104 (2004)
- 2 Hellio, C and Yebra, DM, *Advances in marine antifouling coatings and technologies*. Woodhead Publishing Limited, Cambridge, UK (2009)
- 3 Lejars, M, Margaillan, A and Bressy, C, "Fouling Release Coatings: A Nontoxic Alternative to Biocidal Antifouling Coatings." *Chemical Reviews*, 112 (8) 4347-4390 (2012)
- 4 Nurioglu, AG, Esteves, ACC and de With, G, "Non-toxic, non-biocide-release antifouling coatings based on molecular structure design for marine applications." *Journal of Materials Chemistry B*, 3 (32) 6547-6570 (2015)
- 5 Callow, JA and Callow, ME, "Trends in the development of environmentally friendly fouling-resistant marine coatings." *Nat Commun*, 2 244 (2011)
- 6 Magin, CM, Cooper, SP and Brennan, AB, "Non-toxic antifouling strategies." *Materials Today*, 13 (4) 36-44 (2010)
- 7 Schultz, MP, Bendick, JA, Holm, ER and Hertel, WM, "Economic impact of biofouling on a naval surface ship." *Biofouling*, 27 (1) 87-98 (2011)
- 8 Callow, ME and Callow, JA, "Marine biofouling: a sticky problem." *Biologist*, 49 (1) 10 (2002)
- 9 Konstantinou, IK and Albanis, TA, "Worldwide occurrence and effects of antifouling paint booster biocides in the aquatic environment: a review." *Environment International*, 30 (2) 235-248 (2004)

- 10 Partha, M, Abdullah, E and Dean, CW, "Thermoset Siloxane - Urethane Fouling Release Coatings." Smart Coatings, pp. 61-75. American Chemical Society, (2007)
- 11 Webster, DC and Ekin, A, "Functionalized Polysiloxane Polymers." US 7799434 B2, 2010.
- 12 Webster, DC, Pieper, RJ and Ekin, A, "Thermoset Siloxane-Urethane Fouling Release Coatings." US 7989074 B2, 2011.
- 13 Ekin, A and Webster, DC, "Combinatorial and High-Throughput Screening of the Effect of Siloxane Composition on the Surface Properties of Crosslinked Siloxane-Polyurethane Coatings." Journal of Combinatorial Chemistry, 9 (1) 178-188 (2006)
- 14 Bodkhe, RB, Thompson, SEM, Yehle, C, Cilz, N, Daniels, J, Stafslie, SJ, Callow, ME, Callow, JA and Webster, DC, "The effect of formulation variables on fouling-release performance of stratified siloxane-polyurethane coatings." Journal of Coatings Technology Research, 9 (3) 235-249 (2012)
- 15 Sommer, S, Ekin, A, Webster, DC, Stafslie, SJ, Daniels, J, VanderWal, LJ, Thompson, SEM, Callow, ME and Callow, JA, "A preliminary study on the properties and fouling-release performance of siloxane-polyurethane coatings prepared from PDMS macromers." Biofouling, 26 (8) 961-972 (2010)
- 16 Iguerb, O, Poleunis, C, Mazéas, F, Compère, C and Bertrand, P, "Antifouling Properties of Poly(methyl methacrylate) Films Grafted with Poly(ethylene glycol) Monoacrylate Immersed in Seawater." Langmuir, 24 (21) 12272-12281 (2008)
- 17 Wyszogrodzka, M and Haag, R, "Synthesis and Characterization of Glycerol Dendrons, Self-Assembled Monolayers on Gold: A Detailed Study of Their Protein Resistance." Biomacromolecules, 10 (5) 1043-1054 (2009)

- 18 Andrade, JD, King, RN, Gregonis, DE and Coleman, DL, "Surface characterization of poly(hydroxyethyl methacrylate) and related polymers. I. Contact angle methods in water." *Journal of Polymer Science: Polymer Symposia*, 66 (1) 313-336 (1979)
- 19 Heuberger, M, Drobek, T and Spencer, ND, "Interaction Forces and Morphology of a Protein-Resistant Poly(ethylene glycol) Layer." *Biophysical Journal*, 88 (1) 495-504 (2005)
- 20 Jeon, SI, Lee, JH, Andrade, JD and De Gennes, PG, "Protein—surface interactions in the presence of polyethylene oxide." *Journal of Colloid and Interface Science*, 142 (1) 149-158 (1991)
- 21 Szleifer, I, "Polymers and proteins: interactions at interfaces." *Current Opinion in Solid State and Materials Science*, 2 (3) 337-344 (1997)
- 22 Prime, KL and Whitesides, GM, "Adsorption of proteins onto surfaces containing end-attached oligo(ethylene oxide): a model system using self-assembled monolayers." *Journal of the American Chemical Society*, 115 (23) 10714-10721 (1993)
- 23 Sundaram, HS, Cho, Y, Dimitriou, MD, Weinman, CJ, Finlay, JA, Cone, G, Callow, ME, Callow, JA, Kramer, EJ and Ober, CK, "Fluorine-free mixed amphiphilic polymers based on PDMS and PEG side chains for fouling release applications." *Biofouling*, 27 (6) 589-602 (2011)
- 24 Sundaram, HS, Cho, Y, Dimitriou, MD, Finlay, JA, Cone, G, Williams, S, Handlin, D, Gatto, J, Callow, ME, Callow, JA, Kramer, EJ and Ober, CK, "Fluorinated Amphiphilic Polymers and Their Blends for Fouling-Release Applications: The Benefits of a Triblock Copolymer Surface." *ACS Applied Materials & Interfaces*, 3 (9) 3366-3374 (2011)
- 25 Bodkhe, RB, Stafslie, SJ, Cilz, N, Daniels, J, Thompson, SEM, Callow, ME, Callow, JA and Webster, DC, "Polyurethanes with amphiphilic surfaces made using telechelic functional PDMS having orthogonal acid functional groups." *Progress in Organic Coatings*, 75 (1–2) 38-48 (2012)

- 26 Martinelli, E, Sarvothaman, MK, Galli, G, Pettitt, ME, Callow, ME, Callow, JA, Conlan, SL, Clare, AS, Sugiharto, AB, Davies, C and Williams, D, "Poly(dimethyl siloxane) (PDMS) network blends of amphiphilic acrylic copolymers with poly(ethylene glycol)-fluoroalkyl side chains for fouling-release coatings. II. Laboratory assays and field immersion trials." *Biofouling*, 28 (6) 571-582 (2012)
- 27 Imbesi, PM, Finlay, JA, Aldred, N, Eller, MJ, Felder, SE, Pollack, KA, Lonnecker, AT, Raymond, JE, Mackay, ME, Schweikert, EA, Clare, AS, Callow, JA, Callow, ME and Wooley, KL, "Targeted surface nanocomplexity: two-dimensional control over the composition, physical properties and anti-biofouling performance of hyperbranched fluoropolymer-poly(ethylene glycol) amphiphilic crosslinked networks." *Polymer Chemistry*, 3 (11) 3121-3131 (2012)
- 28 Stafslie, SJ, Christianson, D, Daniels, J, VanderWal, L, Chernykh, A and Chisholm, BJ, "Combinatorial materials research applied to the development of new surface coatings XVI: fouling-release properties of amphiphilic polysiloxane coatings." *Biofouling*, 31 (2) 135-149 (2015)
- 29 Webster, DC and Bodkhe, RB, "Functionalized silicones with polyalkylene oxide side chains." US 9169359 B2, 2015.
- 30 Casse, F, Ribeiro, E, Ekin, A, Webster, DC, Callow, JA and Callow, ME, "Laboratory screening of coating libraries for algal adhesion." *Biofouling*, 23 (3/4) 267-276 (2007)
- 31 Cassé, F, Stafslie, SJ, Bahr, JA, Daniels, J, Finlay, JA, Callow, JA and Callow, ME, "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 (2) 121-130 (2007)
- 32 Callow, ME, Callow, JA, Conlan, S, Clare, AS and Stafslie, S, "Efficacy testing of nonbiocidal and fouling-release coatings." *Biofouling Methods*, pp. 291-316. John Wiley & Sons, Ltd, (2014)

- 33 Stafslie, SJ, Bahr, JA, Daniels, JW, Wal, LV, Nevins, J, Smith, J, Schiele, K and Chisholm, B, "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." *Review of Scientific Instruments*, 78 (7) 072204 (2007)
- 34 Rittschof, D, Orihuela, B, Stafslie, S, Daniels, J, Christianson, D, Chisholm, B and Holm, E, "Barnacle reattachment: a tool for studying barnacle adhesion." *Biofouling*, 24 (1) 1-9 (2008)
- 35 Stafslie, S, Daniels, J, Bahr, J, Chisholm, B, Ekin, A, Webster, D, Orihuela, B and Rittschof, D, "An improved laboratory reattachment method for the rapid assessment of adult barnacle adhesion strength to fouling-release marine coatings." *Journal of Coatings Technology and Research*, 9 (6) 651-665 (2012)
- 36 Owens, DK and Wendt, RC, "Estimation of the surface free energy of polymers." *Journal of Applied Polymer Science*, 13 (8) 1741-1747 (1969)
- 37 Baier, RE, "Surface behaviour of biomaterials: The theta surface for biocompatibility." *Journal of Materials Science : Materials in Medicine*, 17 (11) 1057-62 (2006)
- 38 Louette, P, Bodino, F and Pireaux, J-J, "Poly(dimethyl siloxane) (PDMS) XPS Reference Core Level and Energy Loss Spectra." *Surface Science Spectra*, 12 (1) 38 (2005)
- 39 Mishra, AK, Chattopadhyay, DK, Sreedhar, B and Raju, KVS, "FT-IR and XPS studies of polyurethane-urea-imide coatings." *Progress in Organic Coatings*, 55 (3) 231-243 (2006)
- 40 Hearn, MJ, Ratner, BD and Briggs, D, "SIMS and XPS studies of polyurethane surfaces. 1. Preliminary studies." *Macromolecules*, 21 (10) 2950-2959 (1988)
- 41 Majumdar, P, Lee, E, Patel, N, Ward, K, Stafslie, SJ, Daniels, J, Chisholm, BJ, Boudjouk, P, Callow, ME, Callow, JA and Thompson, SEM, "Combinatorial materials research applied to the development of new surface coatings IX: An investigation of

- novel antifouling/fouling-release coatings containing quaternary ammonium salt groups." *Biofouling*, 24 (3) 185-200 (2008)
- 42 Hoipkemeier-Wilson, L, Schumacher, JF, Carman, ML, Gibson, AL, Feinberg, AW, Callow, ME, Finlay, JA, Callow, JA and Brennan, AB, "Antifouling potential of lubricious, micro-engineered, PDMS elastomers against zoospores of the green fouling alga *Ulva* (*Enteromorpha*). " *Biofouling*, 20 (1) 53-63 (2004)
- 43 M.E Callow, JAC, L.K Ista, S.E Coleman, A.C Nolasco, G.P Lopez, "Use of self assembled monolayers of different wettabilities to study surface selection and primary adhesion processes of green algae (*Enteromorpha*) zoospores." *Applied and Environmental Microbiology*, 66 (8) 3249-3254 (2000)
- 44 Finlay, JA, Callow, ME, Ista, LK, Lopez, GP and Callow, JA, "The Influence of Surface Wettability on the Adhesion Strength of Settled Spores of the Green Alga *Enteromorpha* and the Diatom *Amphora*." *Integrative and Comparative Biology*, 42 (6) 1116-1122 (2002)
- 45 J.A Callow, MEC, L.K Ista, G Lopez, M.K Chaudhury, "The influence of surface energy on the wetting behavior of the spore adhesive of marine alga *Ulva linza*." *Journal of Royal Society Interface*, 2 319-325 (2005)
- 46 Holland, R, Dugdale, TM, Wetherbee, R, Brennan, AB, Finlay, JA, Callow, JA and Callow, ME, "Adhesion and motility of fouling diatoms on a silicone elastomer." *Biofouling*, 20 (6) 323-329 (2004)
- 47 Petrone, L, Di Fino, A, Aldred, N, Sukkaew, P, Ederth, T, Clare, AS and Liedberg, B, "Effects of surface charge and Gibbs surface energy on the settlement behaviour of barnacle cyprids (*Balanus amphitrite*). " *Biofouling*, 27 (9) 1043-1055 (2011)

Supplemental Information

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

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

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

F8

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

S2: Compositions of pre-polymers investigated during this study

Pre-polymer	Wt of IPDI trimer (g)	Starting NCO Eq.	MW of PDMS (g/mol)	Wt of PDMS (g)	OH Eq. from PDMS (X ₂)	MW of PEG (g/mol)	Wt of PEG (g)	OH Eq. from PEG (X ₃)	EEP (g)	Ending NCO Eq. (X ₁)
IPDI-5-1kPDMS-550PEG	1.7152	3.38E-03	1000	0.8000	8.00E-04	550	0.8000	1.45E-03	1.6000	1.13E-03
IPDI-5-5kPDMS-550PEG	1.2283	2.42E-03	5000	0.8000	1.60E-04	550	0.8000	1.45E-03	1.6000	8.08E-04
IPDI-5-10kPDMS-550PEG	1.1675	2.30E-03	10000	0.8000	8.00E-05	550	0.8000	1.45E-03	1.6000	7.68E-04
IPDI-5-1kPDMS-750PEG	1.4199	2.80E-03	1000	0.8000	8.00E-04	750	0.8000	1.07E-03	1.6000	9.33E-04
IPDI-5-5kPDMS-750PEG	0.9330	1.84E-03	5000	0.8000	1.60E-04	750	0.8000	1.07E-03	1.6000	6.13E-04
IPDI-5-10kPDMS-750PEG	0.8722	1.72E-03	10000	0.8000	8.00E-05	750	0.8000	1.07E-03	1.6000	5.73E-04
IPDI-10-1kPDMS-550PEG	3.4299	6.76E-03	1000	1.6000	1.60E-03	550	1.6000	2.91E-03	1.6000	2.25E-03
IPDI-10-5kPDMS-550PEG	2.4567	4.84E-03	5000	1.6000	3.20E-04	550	1.6000	2.91E-03	1.6000	1.62E-03
IPDI-10-10kPDMS-550PEG	2.3351	4.60E-03	10000	1.6000	1.60E-04	550	1.6000	2.91E-03	1.6000	1.54E-03
IPDI-10-1kPDMS-750PEG	2.8400	5.60E-03	1000	1.6000	1.60E-03	750	1.6000	2.13E-03	1.6000	1.87E-03
IPDI-10-5kPDMS-750PEG	1.8663	3.68E-03	5000	1.6000	3.20E-04	750	1.6000	2.13E-03	1.6000	1.23E-03
IPDI-10-10kPDMS-750PEG	1.7446	3.44E-03	10000	1.6000	1.60E-04	750	1.6000	2.13E-03	1.6000	1.15E-03

S3: AFM height images for AmSiPU coatings

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

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

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