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Hydrophilic silicone coatings as fouling release: Simple synthesis, comparison to commercial, marine coatings and application on fresh water-cooled heat exchangers

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Abstract

A synthesis route to hydrophilic, biocide-free fouling-release coatings by dispersing a polydimethyl siloxane (silicone, PDMS)-polyethylene glycol (PEG) copolymer in a PDMS coating is described. In comparison to known coatings including commercial fouling release for marine vessels, anti-fouling and fouling release performance was investigated by laboratory tests (contact angle, pseudo barnacle test and bacteria culture test applying *Pseudomonas aeruginosa*) and by application on fresh water-cooled surface condensers mimicking conditions of thermal power plants. A developmental silicone coating comprising PEG reduced fouling growth and adhesion in laboratory tests by more than a factor of ten compared to steel. In a freshwater exposure test, a comparative, commercial fouling release coating performed better than the developmental PEG-PDMS coating and is a promising candidate for applications on surface condensers of thermal power plants as it reduces fouling at a flow rate of just 1.6 m/s.

1 Introduction

The present research was motivated by the potential application of coatings to reduce biofouling in surface condensers (heat exchangers in thermal power plants) applying sea or fresh water as coolant. The accumulation of bacteria, algae or animals affects pressure drop and heat transfer; potential growth of pathogenic bacteria is a health and legislative concern. Today, power plants tolerate a certain loss in effectivity, and thus a higher than necessary water consumption, due to biofouling. Alternatively, water with biocides like chlorine or monochloramine, or a sponge-ball cleaning system are applied. Hygiene laws may require disinfection of cooling water before feeding into rivers or lakes. Surface condensers typically provide a flow rate around 2 m/s, temperatures of 27 to 40°C, and set a limit for coating thickness. As a rule of thumb, coatings above 10 µm will reduce heat transfer by more than 10% [1], which might not necessarily be compensated by a fouling reduction gain. Interest in fouling reduction arises also from the aim to apply unconventional cooling water, such as industrial waste water, in areas with water scarcity [2]. As coating of surface condensers is not common, we discuss below related applications to combat biofouling on marine vessels or medical equipment, which have inspired both development of a biocide-free, silicone-polyethylene glycol fouling-release coating for heat exchanges and selection of known, comparative coating solutions against fouling.

Biofouling comprises the sequential stages of the absorption of proteins, glycoproteins, polysaccharides, lignin-derived materials or inorganic matter to form a conditioning film; the growth of pioneering single cell organisms such as bacteria or diatoms; the formation of a microfouling slime film from further single cell and first multicellular species such as spores of macroalgae; and the formation of macrofouling by macroalgae, mollusks and various other species [3,4,5,6].

In the past, to avoid biofouling on marine vessels, anti-fouling coatings were applied almost exclusively and are still the preferred choice for military and leisure boats that stay for long periods in the harbor as they are effective at low flow rates or even without flow [5,7]. On merchant ships and ferries, fouling release coatings can be applied. They do not necessarily prevent the growth of fouling and often tolerate a thin slime layer [7], but provide low fouling adhesion and allow the flow to detach larger macrofouling. They are non-sacrificial, and typically free of biocides, although combinations of fouling release and anti-fouling exist [8,9,10,11].

Most commercial fouling release coatings are based on silicone rubber (cross-linked polydimethylsiloxane, PDMS) [5,12], or copolymers comprising PDMS [13,14,15]. As proposed by adhesion theories [5,16,17,18], these coatings provide low fouling adhesion by providing a smooth surface, thus no interlocking can occur, avoiding penetration by microorganisms and providing a low elastic modulus. However, the low surface tension of the hydrophobic PDMS is not advantageous, which is attributed to the especially low Lewis acid and base contributions [19] to the three-component model for interfacial tension [20,21]. Water provides exceptionally high Lewis acid and base contributions [22] compared to PDMS and to typical biomolecules [22,23], which leads to high interfacial tension between water and PDMS and between water and fouling, high energy for water to penetrate the fouling/PDMS interface and thus high fouling/PDMS adhesion. To provide a hydrophilic surface and thus a low coating-to-water interfacial tension, many modern fouling release coatings consist of silicone rubber with hydrophilic additives. The hydrophilic surfaces both facilitate fouling release and reduce the initial growth of fouling [6,24]. Most widely applied are additives based on polyethylene glycol (PEG) copolymers

[9,13,14,15,25,26,27,28]. The low bio-adhesion of PEG is well documented [29,30]. PEG is hydrophilic and acts especially as Lewis base, which is advantageous for fouling removal [31].

PEG-containing coatings differ in how PEG or a PEG copolymer are bound to silicone rubber. One option is chemical bonding, supposedly stable under exposure conditions [9,13,14,15,25,28]. Another option is no chemical bonding, but solely a blend of PEG copolymers and silicone rubber [9,27]. A third option is chemical bonding by a hydrolysable bond between a silicon atom of the respective cross-linker, for example tetraethyl orthosilicate, and a terminal OH group of a PEG chain [10,26]. There is limited information available, as to whether stable crosslinking is an advantage in order to avoid leaching of the respective hydrophilic component, or whether hydrophilic components that are not crosslinked or where the link is easy to hydrolyze are advantageous by providing higher mobility for the PEG moiety to diffuse to the coating surface when in contact with water. Besides PEG, polymers comprising organic salts are applied [30,32]. Generally speaking, hydrophilic fouling release coatings require a specific drag that is typically reached at cruise speeds of 7-10 knots (ca. 3.6-5.1 m/s) or even higher [5,7]. However, for a silicone-PEG-perfluoropolymer coating, a part removal of fouling at 1-1.5 m/s and complete slime removal above 3.1 m/s is claimed [26,33].

To avoid aggregation of bacteria, cells or blood on medical and laboratory equipment, a vast amount of research has been carried out that goes beyond the scope of this publication and has lead to the commercialization of single coatings [34,35,36]. Most coatings have common features with marine fouling release coatings in that they provide a hydrophilic surface by applying non-ionic polymers such as PEG or PVP and/or organic salts (polyelectrolytes). Besides silicone rubber, also other base materials, for example modified acrylates, or silane-monolayers are applied [29,30,37].

As a further alternative to biocidal coatings, enzyme-containing coatings have been proposed as environmentally friendly options for marine, medical or food applications [5,38,39,40,41]. Enzymes have been proven to maintain activity within a coating, if the coating matrix provides an adequate environment. A commonly applied enzyme is subtilisin, which is expected to hydrolyze proteins and thus break down the extracellular matrix that supports bacteria adhesion and growth.

Herein, we describe the synthesis of silicone rubber coatings comprising varying amounts of PEG, following the hydrolysable-silane bond-approach described above. The coatings were compared to reference coatings, including commercial fouling release and enzyme coatings, by contact angle measurements, by a laboratory fouling growth test applying *Pseudomonas aeruginosa*, by pseudo barnacle test (PBT) monitoring fouling release in the laboratory, and finally by exposing coated tubes and strips in heat exchangers to conditions simulating power plants using fresh water as coolant.

2 Materials and Methods

2.1 Base materials

Algae culture test: cylindric glass inserts (Hirschmann, l: 40 mm, d: 6.5 mm), additional samples prepared from AISI 316L steel pipe (RS components, d: 6.8 mm). *Contact angle measurements:* AISI 316L steel sheet (Sanistål, d: 1.5 mm, cut to 75 x 25 mm). *Pseudo barnacle test:* same as contact angle, but size 100 x 200 mm. *Fouling test in surface condenser:* AISI 316L steel tubes, l: 150 mm, ID 16 mm, OD: 18 mm. *Water jet test:* AISI 316L steel stripes, 305 x 18 mm.

All stainless steel samples were alkaline cleaned in a 10% solution of Tickopur TR 13 (Dr.H. Stamm) for 3 min at 60-70°C in an ultrasonic bath, rinsed with water and dried 10 min at 105°C, except where stated otherwise. Glass was rinsed with acetone.

2.2 Coatings

Glass inserts and tubes were flush-coated by filling and letting coating run. All other materials were spray-coated except that Primer 2 and FR1 were applied by paint brush, and Primer 4 and all Enzy coatings were applied by dip-coating. All coatings were cured 24 h at ~20°C unless stated otherwise.

Primer 1: Blend of 9 g Silic One Tie coat (Hempel) and 11 g methyltriethoxysilane (as solvent), dry film thickness (DFT) 2-3 µm.

Primer 2: First layer proprietary epoxy cured 1 h at 140°C, DFT ~5 µm, second layer Silic One Tie coat (Hempel), DFT ~20-40 µm.

Primer 3: Hempasil XA714 (Hempel, blend of 70.7 g Base XA715, 11.5 g Hardener XA418 and 7.8 g Additive XA716) with additional 10 g toluene. Applied within 15 min after mixing to prevent sagging, cured 18 h at 20°C, DFT 20-50 µm (steel sheet), 35-

Primer 4: Proprietary inorganic sol-gel primer, cured at 250°C, DFT <1 µm.

Si: Blend of 100 g silan-terminated PDMS, M ~18000 g/mol (Gelest DMS-S27) with 25 g bis(triethoxysilylpropyl)amine, stirred 20 h at 20°C, then addition of 2 g of a 75% solution of zinc neodecanoate in heavy, hydrotreated naphtha (OMG Borch Kat 15) and 127 g methyltriethoxysilane (as solvent), DFT 7-10 µm, except samples for pseudo barnacle test (PBT) 30-40 µm, no primer for glass inserts and CA-samples, all other samples applied on Primer 3.

Si2: Like Si, but using 1.5 g dibutyltin dilaurate (DBTL) instead of Borch Kat 15.

SiPEG2, 3.3, 6.7, 13.3, 20, 20i and 26.7: Hydrophilic silicone rubber. Prepared like Si with the only difference, that instead of 127 g methyltriethoxysilane, only 94.3 g were added. Thereafter addition of 89.9 g absolute ethanol and 3.9 g, 6.7 g, 14.3 g, 32.5 g, 57 g, or 91 g, respectively, of a hydroxyl-terminated PEG-PDMS-PEG triblock copolymer, M 3500-4000 g/mol, 60% PEG/40% PDMS (Gelest DBE-C25) followed by effective magnetic stirring to obtain a fine dispersion for 2 h. Stirred prior to application and applied within 1 h avoid phase separation, DFT 5-10 µm (glass inserts), 4-5 µm (12/12i on steel sheet), ~10 µm (12/12i on steel tubes) or 8-11 µm (all except 12/12i on steel), applied on top of Primer 3. The number in the coating name (2 to 26.7) indicates the percentage of PEG based on total coating solids. 20i is identical to 20, but applied on top of Primer 4. Amounts of solvents were empirically determined to let the otherwise milky suspension appear almost clear, which also happens at a ratio of 84.7 g methyltriethoxysilane and 66.8 g ethanol.

SiOxim: Prepared by stirring 90 g silan-terminated PDMS, ~18000 g/mol (Gelest DMS-S27) with 10 g vinyltris(methylethylketoximinio)silane (Gelest) and 22 g dry butylacetate for 20 h at 20°C. Cured 48 h at 20°C. Glass inserts: DFT 20-25 µm, no primer. Steel: DFT 5-7 µm, on top of Primer 3.

Siwet, SiOximwet, SiPEG2, 3.3, 6.7, 13.3, 20 and 26.7wet. Prepared like the respective Si, SiOxim and SiPEG coatings, but cured for 5 min at 20°C and then immersed in water at 20°C for ~18 h, thereafter stored dry.

Epoxy: Blend of 100 g EP 200-90 2K Top Coat gloss (Mipa, pigmented solution of a bisphenol A-based epoxy resin, Mn 700-1100 g/mol), 25 g EP 950-25 2K-EP-hardener (Mipa, solution of a polyaminoamide adduct) and 45 g 1-methoxy-2-propanol, cured 1 h at 140°C, DFT 5-20 µm (glass inserts) or 20-25 µm (steel).

FR1 and Fr1thin: Silic one (Hempel), FR1 without dilution, glass inserts: DFT 50-80 µm, applied on Primer 1, on steel: DFT 70-100 µm, applied on Primer 2. FR1thin diluted with 1.22 g methyltriethoxysilane (as solvent) per 1 g Silic One, DFT 2-3 µm, no primer.

FR2: Hempasil XA637 (Hempel, blend of 62.1 g Base 87509 and 7.9 g Hardener XA 632) with additional 30 g toluene, applied within 15 min after mixing to prevent sagging, DFT 5-10 µm (glass inserts), 10-15 µm (steel for contact angle measurements (CA)), 20-50 µm (all other steel sheet) and 75-90 µm (steel tubes), applied on top of Primer 3.

SolGel1, SolGel1H: Previously published [42] as examples 2 and 1, respectively, additionally diluted with 0.3 g ethanol and 0.3 g 4-methyl-2-pentanone per 1 g coating, cured 1 h at 200°C. DFT 2-5 µm. Both coatings differ by solely SolGel1H providing a PDMS-additive to render the surface more hydrophobic.

SolGel2a, b and c: Proprietary organic-inorganic hybrid sol-gel coatings, cured 2.5 h at 200°C (c) or 300°C (a,b). DFT ~2 µm (a) or ~1 µm (b,c).

Enzy, EnzyDenat and EnzyRef: Sol-gel coating as previously published [40], with the difference for Enzy that instead of 0.2 ml of a subtilisin solution as published, both 0.2 ml of a lysozyme solution (32 U/ml = 0.8 µg/ml) in phosphate buffered saline pH 7.4 (PBS), 0.25 ml ethanol and 0.3 ml water were added. EnzyDenat was prepared like Enzy, but the lysozyme solution was denatured by heating to 90°C for 30 min. EnzyRef was prepared like Enzy, but instead of lysozyme in PBS, solely PBS without enzyme was added. DFT 5-10 µm (glass inserts) or 7-13 µm (steel).

2.3 Characterization

Coating thickness was measured by eddy current probe (Byk-Gardener Bykotest 7500) on at least three spots per specimen. Thickness on glass and steel tubes was estimated by measuring an aluminum coupon coated in the same way and is expected to result in a comparable coating thickness.

Contact angles (CA) were determined on at least five spots per specimen using a DSA 10 (Krüss) at 20-23°C. Static CA were determined by software from images of sessile drops with a volume of ~5 µl. For coatings where the baseline of the applied drop significantly expands, typically coatings with hydrophilic moieties orienting towards the surface, a static CA was determined again directly after baseline expansion, which is usually after 1-3 min. Advancing and receding CA were determined by increasing or reducing drop volume until the baseline of the drop expanded or contracted, and due to lack of video recording, determined from an image recorded about 1 s after the drop came to halt. This technique may lead to advancing CA being 0-2° lower, and receding CA being 0-5° higher than the actual 'static advancing' and 'static receding' CA measured just before the baseline expands or contracts. CA of drops not recognized by the software were determined manually using an angle meter.

Fouling adhesion was estimated by a pseudo barnacle test (PBT), each result is based on six measurements (three on each two coating specimen). Aluminum studs, d=20 mm were glued

onto the coated plates using the two-component epoxy adhesive UHU Plus sofortfest (UHU), cured 10 min at 90°C and were after cooling to below 30°C vertically pulled off with a Positest AT-A (DeFelsko) at a rate of 0.2 MPa/s. The adhesive was chosen to allow fast curing for repeated testing on the same spots.

Biofilm growths at laboratory scale was evaluated by a partly automated test modified from a previously published protocol [43], applying a culture of the gram-negative bacteria *Pseudomonas aeruginosa*, followed by dying and photometric quantification of recovered dye from those cells that adhere to the coating. Prior to testing, all surfaces were sterilized by UV-light for 30 min under laminar flow. Instead of Crystal Violet, which interacted with some of the coatings, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was used as the indicator dye. MTT is reduced by metabolically active bacteria to a blue formazan, which can be measured at 540 nm. Thus, any bound, unreduced, yellow MTT dye does not influence the results. Two test runs on each six coating samples were carried out. From one test run to another, due to the stacking of variabilities in biofilm growth, washing, dying and dye recovery, the absolute amount of recovered dye may differ significantly. Therefore, not the absolute amounts of biofilm are provided, but biofilm attached to the epoxy coating is used as reference and set to 100%. The other surfaces are compared relative to this reference.

Biofilm growth was also investigated in a test loop mimicking power plant conditions according to Figure 1. The loop comprises a steam condenser with seven tubes of 2 m length and 16 mm diameter. Some of the tubes located at the outlet of the condenser consist of connected, 150 mm long tube parts coated on the inner diameter. The outer diameter of the condenser tubes is warmed by a low-pressure boiler generating steam. As the tubes are serially connected, there is a gradient in the first tube from basin temperature to 40°C, while the later tubes, which comprise the test samples, all remain at approximately 40°C. The flow is 1.6 m/s. The test was carried out in two runs. Run 1, starting October 10, 2017, applied water from the river Seine in Chatou, France, and applied an automatic addition of sulfuric acid to avoid limescale. Run 2 started February 27, 2018, applying a solution of 7.5% Seine water in demineralized water, addition of acid is not necessary. After passing the heat exchanger, the water passes a cooling tower filled with PVC sheets. The evaporated water is thereafter replaced with fresh river water or the blend of demineralized water and river water, respectively. The amount of sediment and bacteria in the river water changes significantly over time; tests require steel references for comparison. Several coatings and stainless steel references were tested in the same loop by mounting the up to 12 tube parts per coating in alternating order. Run 1 was interrupted weekly to remove a neighboring section of one tube part for each coating and replace it with a steel pipe. The removed parts were rinsed with sterile, demineralized water. Any fouling was dispersed in 150-200 ml sterile, demineralized water by gentle brushing and sonication for 10 min. According to standardized procedures, dry matter content was determined by drying at 105°C and weighing [44], total bacteria count [45] and Legionella count [46] by cultivation and counting using a microscope. At the end of the test runs, three instead of one tube per coating were analyzed.

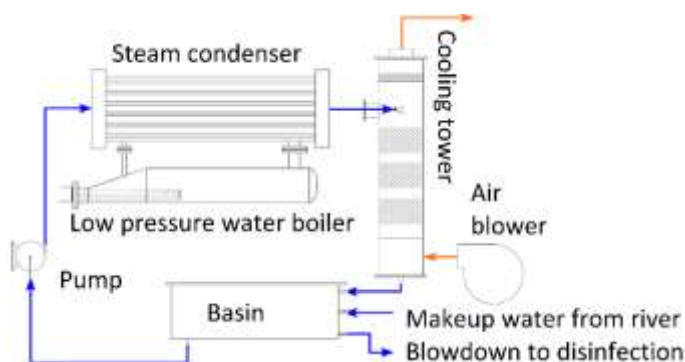


Figure 1: Fouling test loop

Fouling adhesion was investigated on metal stripes mounted into the tubes, thus exposed to identical flow and temperature. After exposure, the stripes were cleaned by driving a nozzle with a speed of 56 mm/s over the specimen, applying a flat water jet vertical to the sample, adjusted to a specific pressure. Per test run and coating, two specimen were investigated at three different pressures.

3 Results and discussion

3.1 *Silicone-PEG coating synthesis and selection of comparative reference surfaces*

The coatings SiPEG2 to 26.7, which main components are shown in Figure 2, lead to PDMS-based coatings presenting a PEG-based hydrogel surface. The coatings differ from most comparable, previous PDMS-PEG approaches in that they connect PEG to PDMS by a hydrolysable bond, and differ from those approaches also providing a hydrolysable bond between PEG and PDMS by providing systematic variation of the PEG content, a low film thickness of 10 μm or less and the application of a fluorine-free, hydroxyalkyl-terminated silicone-PEG copolymer instead of pure PEG [10], PEG-fatty alcohol ethers [10] or PEG-perfluoropolyether copolymers [26]. The ethanol/methyltriethoxysilane solvent blend allows a temporarily stable emulsion of the PEG-PDMS copolymer in a PDMS solution to be obtained, which, upon standing, separates within a day. While not monitored by chemical analysis, we expect the terminal carbinol OH of PEG-PDMS to exchange to some extent with ethoxy groups of the bis[3-(triethoxysilyl)propyl]amine crosslinker [47] and thus be chemically cross-linked after curing by a hydrolysable bond. Due to its significantly lower reactivity as compared to aminopropylsilanes [48], and lower boiling point, we expect methyltriethoxysilane mainly to act as solvent and not to react. Condensation curing conserves the dispersion of PEG-PDMS in PDMS; obtained coatings are hazy. The application of pure PEG instead of the PEG-PDMS did not led to a temporary stable emulsion.

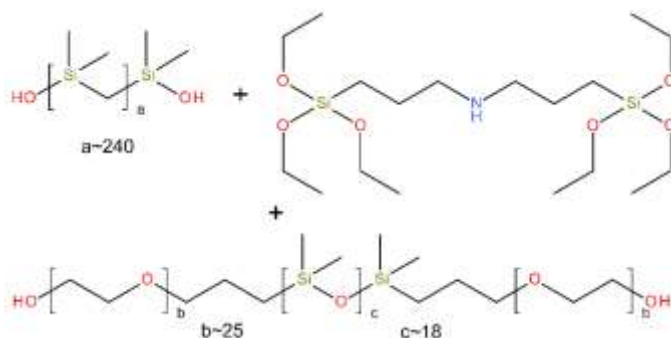


Figure 2: Main components of the SiPEG coatings

Several surfaces were investigated to be able to compare the performance of the SiPEG coatings with steel, glass, silicone rubber (PDMS) without PEG, a commercial epoxy topcoat, Sol-Gel coatings and commercial fouling release (FR) for marine vessels. FR is also based on PDMS/hydrogel. A second PDMS system (SiOxim) was investigated to be able to see potential side effects of catalyst and aminosilane crosslinker of the first system (Si). SolGel1H was applied as it is known to reduce crude oil-derived fouling on heat exchanges [19]. It provides a PDMS surface layer but is, like to other SolGel coatings, harder than silicone rubber. Enzy is a sol-gel coating comprising lysozyme, where the activity of the coating surface was proven by a test reaction. The coating previously reduced bacteria fouling in tests with fresh water [41]. Otherwise identical coatings were tested with denatured enzyme and without enzyme. As previously discussed, coating thickness affects heat transfer [1]. We aimed for the coatings to stay around or below 10 μm for SiPEG, sol-gel and enzyme coatings. For commercial fouling release, thicknesses of several 100 μm are recommended, FR1 was thus applied at 70-100 μm , FR1thin around 2-3 μm and FR2 as a compromise between aim and recommendation at 20-50 μm .

3.2 Contact angle measurements

Water contact angles (CA, θ) as provided by Figure 3, Table 1 and Table 2 show the surface's interactions with water. Hydrophobic surface domains generate high advancing (adv) CA, hydrophilic domains low receding (rec) CA. CA data does not allow conclusion on the size of the domains and is also influenced by surface roughness. Static and, if observed, expanded static CA show whether the surface changes in contact with water. While the surface-water interactions are relevant for fouling initiation, CA data does not represent specific anchor groups for fouling and does, with solely water as test liquid, not differentiate between disperse/dipole and Lewis acid and base surface energy components.

As compared to pure PDMS coatings, the addition of PEG-PDMS renders the surfaces hydrophilic, dependent on PEG concentration (see Figure 3). θ_{rec} decreases, while θ_{adv} stays high, leading to high contact angle hysteresis (CAH), caused by an inhomogeneous surface of both PDMS and PEG domains. In contact with water, the surfaces become more hydrophilic, which is a typical behavior of hydrogel surfaces, usually caused by absorption of water and by orientation of hydrophilic moieties towards the coating surface to reduce the interfacial water-coating energy. The latter happened also for the PEG-free Si system, possibly due to amine groups and/or remaining SiOH groups orientating towards the surface, but not for the SiOxim coating. We have noted in Table 1 and Table 2 when the contact area of droplets applied to measure static contact angles expanded in the first minute. Where the tables mention expansion without a providing the exact expanded CA, the expanded CA is 3-10° lower than the static CA.. For some coatings, this

phenomenon also led to $\theta_{adv} < \theta_{static}$, caused by the longer contact time to measure θ_{adv} as compared to θ_{static} . In contact with air, like during curing, there is no driving force for hydrophilic groups to orientate towards the surface as the hydrophobic PDMS has a lower surface energy. Therefore, a set of coatings was cured in water to potentially achieve a more hydrophilic surface. For low PEG concentrations of 2 and 3.3%, this led to lower θ_{rec} compared to curing in air. For higher PEG concentrations, both air and wet cure led to $\theta_{rec} = 0^\circ$, therefore, wet curing was not further investigated. The wet-cured coatings surprisingly provided higher θ_{adv} , thus higher CAH, and look hazier. This may reflect larger domains of PEG and PDMS as compared to coatings cured in air, or a rougher surface.

Regarding the comparative coatings, the silicone/hydrogel-based FR1 and FR2 show droplet expansion as described for SiPEG, FR1/FR1thin is less hydrophilic with θ_{rec} of $81.5^\circ/74.4^\circ$, FR2 more with $\theta_{rec} = 0^\circ$ and provides with $\theta_{adv} = 75^\circ$ the lowest value of all PDMS-based coatings. Glass is hydrophilic providing low contact angles, PDMS surfaces (Si, SiOxim, SolGel1H) are hydrophobic, providing high values for both θ_{rec} and θ_{adv} , Epoxy, Enzy and the other SolGel coatings are neither distinctively hydrophilic or hydrophobic. Steel is ambiguous in providing high CAH, probably caused by surface roughness, and in being more hydrophilic after ultrasonic cleaning due to removal of hydrophobic impurities or due to interactions with the alkaline silicate cleaner.

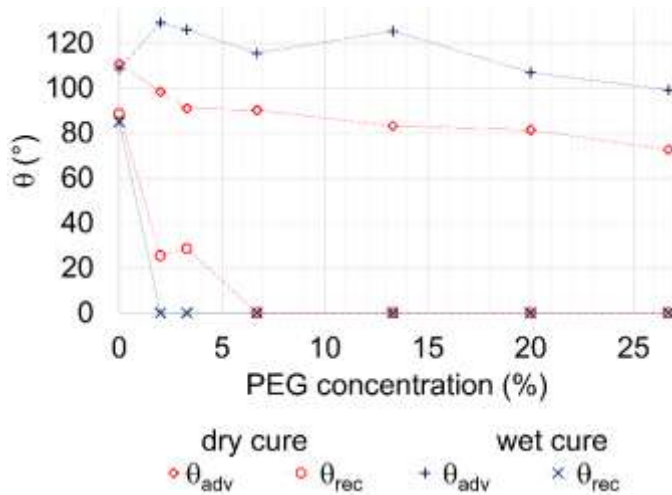


Figure 3: Water contact angles of SiPEG coatings

Table 1: Water contact angles and bacteria fouling test results of SiPEG coatings

Coating	θ (°) (<i>adv.</i> , <i>static</i> , if applicable, <i>static after expansion</i> , <i>rec.</i>)		Relative bacteria count (%) (Epoxy = 100%), dry cure, (<i>combined</i> , <i>1st run</i> , <i>2nd run</i>)
	Dry cure	Wet cure	
Si	<i>a</i> 110.8±1.5	<i>a</i> 108.6±2.5	<i>c</i> 146±42
	<i>s</i> 108.2±2.7	<i>s</i> 107.2±2.3	1 150±59
	<i>e</i> observed	<i>e</i> 100.9±2.6	2 141±20
	<i>r</i> 88.6±2.2	<i>r</i> 85.0±4.1	
SiOxim	<i>a</i> 110.2±1.5	<i>a</i> 110.4±1.8	<i>c</i> 150±16
	<i>s</i> 110.1±1.2	<i>s</i> 108.0±2.8	1 161±16
	<i>r</i> 90.1±0.8	<i>r</i> 90.3±2.9	2 139±7
SiPEG2	<i>a</i> 98.4±8.5	<i>a</i> 129.0±1.2	
	<i>s</i> 108.6±4.3	<i>s</i> 127.7±1.6	
	<i>e</i> observed	<i>e</i> observed	
	<i>r</i> 25.4±6.6	<i>r</i> 0.0±0.0	
SiPEG3.3	<i>a</i> 91.0±1.2	<i>a</i> 126.0±3.0	<i>c</i> 77±19
	<i>s</i> 109.5±0.5	<i>s</i> 125.5±1.5	1 67±22
	<i>e</i> observed	<i>e</i> observed	2 87±9
	<i>r</i> 28.6±2.9	<i>r</i> 0.0±0.0	
SiPEG6.7	<i>a</i> 90.2±2.3	<i>a</i> 115.6±1.8	<i>c</i> 74±12
	<i>s</i> 109.7±1.8	<i>s</i> 126.9±0.4	1 66±7
	<i>e</i> observed	<i>e</i> observed	2 82±10
	<i>r</i> 0.0±0.0	<i>r</i> 0.0±0.0	
SiPEG13.3	<i>a</i> 83.2±4.2	<i>a</i> 125.4±2.1	
	<i>s</i> 107.8±3.1	<i>s</i> 123.2±4.1	
	<i>e</i> observed	<i>e</i> observed	
	<i>r</i> 0.0±0.0	<i>r</i> 0.0±0.0	
SiPEG20	<i>a</i> 81.4±4.7	<i>a</i> 107.0±2.2	<i>c</i> 16±5
	<i>s</i> 109.5±2.9	<i>s</i> 117.4±1.7	1 11±1
	<i>e</i> 41.9±2.4	<i>e</i> 59.1±6.5	2 20±2
	<i>r</i> 0.0±0.0	<i>r</i> 0.0±0.0	
SiPEG26.7	<i>a</i> 72.6±1.6	<i>a</i> 99.2±2.6	
	<i>s</i> 106.3±4.1	<i>s</i> 127.6±1.7	
	<i>e</i> 40.0±4.5	<i>e</i> 55.0±3.3	
	<i>r</i> 0.0±0.0	<i>r</i> 0.0±0.0	

Table 2: Water contact angles and bacteria fouling test results of comparative coatings

Material	θ (°) (<i>adv.</i> , <i>static</i> , if applica- ble, <i>static</i> after <i>expansion</i> , <i>rec.</i>)	Relative bacteria count (%) (Epoxy = 100%), dry cure, (<i>combined</i> , 1 st <i>run</i> , 2 nd <i>run</i>)	Material	θ (°)	Relative bacteria count (%)
steel (acetone cleaned)	<i>a</i> 84.6±7.4 <i>s</i> 86.0±5.0 <i>r</i> 29.0±11.2	<i>c</i> - <i>1</i> - <i>2</i> -	SolGel1H	<i>a</i> 104.7±1.7 <i>s</i> 104.3±1.0 <i>r</i> 93.9±2.4	<i>c</i> 150±53 <i>1</i> 105±8 <i>2</i> 194±35
steel (alkaline cleaned)	<i>a</i> 61.9±7.5 <i>s</i> 59.6±11.2 <i>r</i> 15.1±5.3	<i>c</i> - <i>1</i> 230±13 <i>2</i> -	SolGel1	<i>a</i> 88.4±0.5 <i>s</i> 84.5±1.9 <i>r</i> 71.6±3.0	<i>c</i> 151±30 <i>1</i> 128±22 <i>2</i> 175±10
glass	<i>a</i> 19.6±2.2 <i>s</i> 25.1±3.2 <i>r</i> 5.1±0.9	<i>c</i> 55±10 <i>1</i> 46±2 <i>2</i> 64±4	SolGel2a	<i>a</i> 89.5±1.2 <i>s</i> 84.6±4.6 <i>r</i> 76.2±3.4	<i>c</i> 153±20 <i>1</i> 161±11 <i>2</i> 145±24
Epoxy	<i>a</i> 79.7±3.1 <i>s</i> 76.4±2.9 <i>r</i> 35.3±2.5	<i>c</i> 100 <i>1</i> 100±11 <i>2</i> 100±4	SolGel2b	<i>a</i> 86.8±1.3 <i>s</i> 75.2±2.3 <i>r</i> 56.6±4.1	<i>c</i> 130±37 <i>1</i> 164±6 <i>2</i> 95±5
FR1	<i>a</i> 108.8±5.1 <i>s</i> 112.7±2.8 <i>e</i> 102.6±4.1 <i>r</i> 81.5±5.7	<i>c</i> 41±5 <i>1</i> 18±1 <i>2</i> 56±6	SolGel2c	<i>a</i> 81.9±1.9 <i>s</i> 73.8±2.6 <i>r</i> 54.7±2.6	<i>c</i> 100±37 <i>1</i> 135±7 <i>2</i> 65±4
FR1thin	<i>a</i> 105.1±5.4 <i>s</i> 112.0±3.9 <i>e</i> 101.4±5.6 <i>r</i> 74.4±9.0	<i>c</i> 82±41 <i>1</i> 46±4 <i>2</i> 119±21	Enzy	<i>a</i> 76.2±3.1 <i>s</i> 68.6±2.2 <i>r</i> 48.3±3.3	<i>c</i> 196±61 <i>1</i> 239±51 <i>2</i> 152±32
FR2	<i>a</i> 74.7±9.2 <i>s</i> 66.2±9.8 <i>e</i> 58.5±6.3 <i>r</i> 0.0±0.0	<i>c</i> 41±5 <i>1</i> 44±4 <i>2</i> 38±1	Enzy- denat	<i>a</i> 75.8±3.7 <i>s</i> 69.7±2.1 <i>r</i> 44.1±4.0	<i>c</i> 157±22 <i>1</i> 175±11 <i>2</i> 140±14
			Enzy-buff	<i>a</i> 89.2±1.5 <i>s</i> 89.5±1.4 <i>r</i> 44.3±3.2	<i>c</i> 151±24 <i>1</i> 172±10 <i>2</i> 130±7

3.3 Bacterial culture test

Laboratory tests applying organisms that initiate biofilm formation, such as algae [27] or bacteria can be used to monitor fouling growth. Herein, we applied the Gram-negative bacterium *Pseudomonas aeruginosa* (Figure 4, Table 1 and Table 2) which is relevant as it can initiate biofilm formation in sea and freshwater and is also a pathogen for humans [49,50,51]. As the absolute amount of biofilm growth as monitored by recovered MTT formazan dye can differ significantly from one experimental run to another, the amount of dye recovered from the biofilms formed on the coatings is compared to that of a reference surface, in our case the epoxy coating. Standard deviations of the six samples within one test run are significantly lower than the variability between the two test runs.

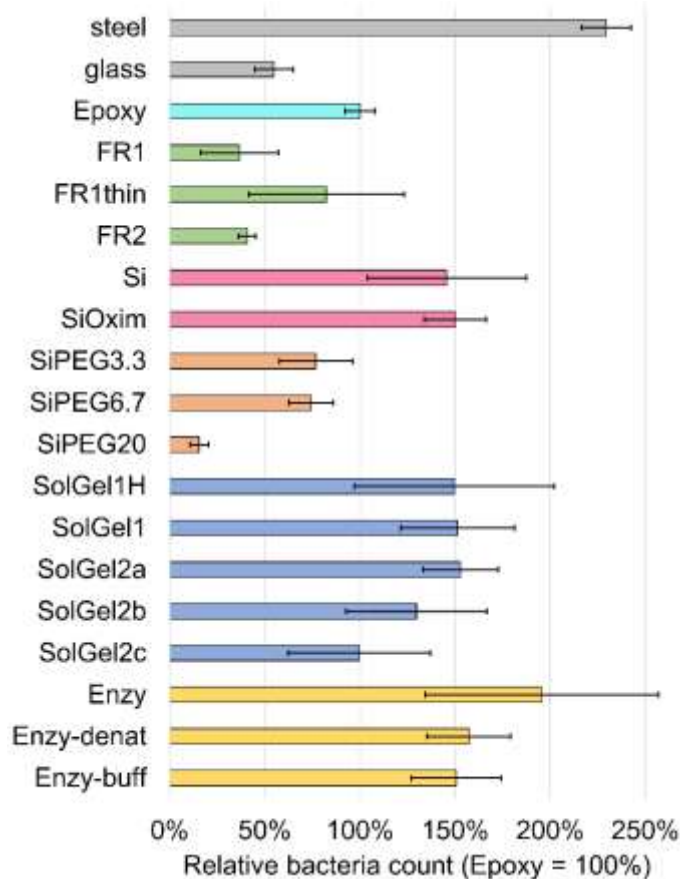


Figure 4: Bacterial culture test applying *Pseudomonas aeruginosa*

The addition of PEG-PDMS reduced bacteria fouling compared to pure PDMS, with 3.3% and 6.7% PEG providing about 50% reduction, while 20% PEG readily reduced bacteria fouling by about 90% compared to pure PDMS and provided lowest fouling of all investigated coatings. SiPEG20 with its higher PEG concentration also provides a significantly lower static contact angle after droplet expansion as SiPEG3.3 and SiPEG6.7, thus a more hydrophilic surface. The effect of PEG-PDMS may be due to the reported low bacteria adhesion to PEG, or due to a biocidal effect. Though PEG-PDMS copolymers are not regarded as aquatic toxic like common biocides, they have been reported to kill bacteria by penetrating their membranes [52].

Compared to the epoxy reference, there is more bacteria fouling on the SolGel and Enzy coatings and on the 316' steel surface. Glass reduces fouling by about 45%, FR1 and FR2 by about 60%. There was about twice as much fouling on the thinner FR1thin coating compared to FR1. As composition is proprietary, we can only speculate that the thinner coating does not provide sufficient reservoir for hydrophilic components. All attempts to add hydrophilic components to silicone rubber (SiPEG3.3, SiPEG6.7, SiPEG20, FR1, FR1thin and FR2) reduced bacteria fouling compared to the unmodified silicone rubbers (Si, SiOxim) and led to droplet expansion when measuring static CA. When taking the whole set of surfaces with their different chemistry into account, there is no obvious relation for a dependence of fouling from any of the collected CA data. All distinctively hydrophilic surfaces providing θ_{rec} of 5° or lower (glass, SiPEG6.7, SiPEG20 and FR2) reduce fouling compared to the Epoxy reference, but to different extents. On the other hand, FR1 reduces fouling without providing low θ_{rec} . We investigated, whether FR1 over time

becomes more hydrophilic by immersing a sample in water for one day, directly followed by rinsing with water without any drying time. The immersed sample was not more hydrophilic.

3.4 *Pseudo barnacle test*

The pseudo barnacle test (PBT) is an umbrella term for tests simulating fouling adhesion. Test conditions to remove living barnacles, well-adherent marine fouling organisms, have been standardized [53]. Following the discovery of Swain et al. [54] who showed that the removal of epoxy studs glued to the dry surface of silicone coatings was easier to carry out and resulted in similar adhesion forces than removal of living barnacles on wet surfaces, the PBT has been applied for various surfaces with different adhesives in both shear and pull-off mode [55,56,57,58]. We have extended the PBT by performing repeated pull-offs on the same spots. A fast-curing epoxy adhesive was applied to avoid unreasonably long testing times.

Initial PBT results are provided by Figure 5. All silicone-based materials and SolGel1 and 1H provided significantly lower adhesion than steel or the epoxy coating. Addition of PEG to PDMS, which changes surface tension, had no significant positive or negative effect on adhesion. Silicone-based, proprietary FR2 provided the lowest adhesion, all studs fell off before reaching the detection threshold of 0.15 to 0.2 MPa. To show a potential degradation of the coating's repellence, seven pull-offs were performed on the same spots for selected surfaces (see Figure 6). Adhesion increases fastest and strongest by a factor of 7-8 for SolGel1H which provides solely a PDMS surface layer that is supposedly more prone to damage than bulk Si or SiPEG20, where adhesion increases slower and only by a factor of 3-5. Compared to initial results for Epoxy or steel, both Si and SiPEG20 still provide significantly lower adhesion, even after seven pull-offs. Proprietary FR2 showed no measurable increase in adhesion, even for the 7th pull-off, all studs fell off before reaching the detection threshold. In real-life applications, barnacles and other organisms repeatedly grow and are removed. A PBT that monitors adhesion after repeated pull-offs is useful by mimicking this repeated removal, especially as our results indeed showed significant differences in the durability of the coating's repellent properties.

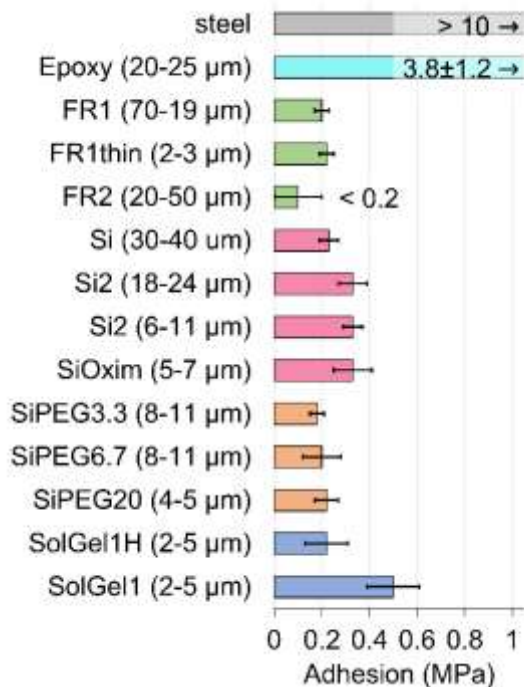


Figure 5: Initial pseudo barnacle adhesion with coating thickness

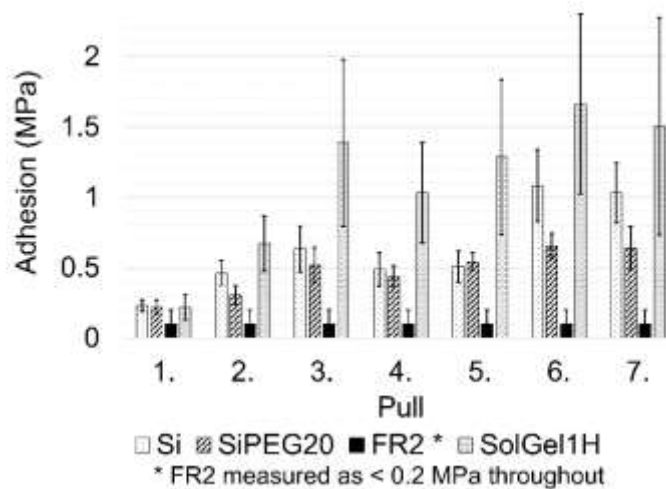


Figure 6: Repeated PBT on the same spots

Conclusions on the effect of the coating's properties on the obtained PBT results are limited. Similar to a previous study [1], our results disagree with established models. While the adhesion of soft fouling seems challenging, models based on fracture propagation for hard fouling like barnacles or epoxy studs on elastomeric coatings have been proposed [5,6,16,17,18,55]. Below, we will compare our results to an accepted concept [6] based on interpretation of fouling and PBT results by Brady [17] to identify possible factors and contradictions.

- *A flexible, linear backbone and low elastic modulus* - SolGel1H has a rigid, cross-linked backbone providing a significantly higher elastic modulus as all silicone-based coatings, but adhesion is as low as for the PDMS based coatings..

- *A backbone that introduces no undesirable interactions* - Possibly in agreement with our results.
- *A sufficient number of surface-active groups which are free to move to the surface and impart a surface energy in the desired range* - Possibly in agreement with our results. The PBT is carried out in air, not in water, thus, a low surface tension (as, for example, provided by PDMS) is advantageous. As outlined in the introduction, in water, PEG would provide a desired surface energy. For SiPEG coatings, CA results indicate both PDMS and PEG at the surface, and also indicate change in contact with water, thus movability. Si and SolGel1H provide solely PDMS at the surface. Densely cross-linked SolGel1H supposedly provides significantly less movability than Si, but it also shows stronger damage after repeated pull-offs than all silicone rubber-based surfaces.
- *A surface which is smooth at molecular level* - Possibly in agreement with our results. Si, SiOxim, SolGel1/1H, FR1/2 surfaces are glossy and for Si, SiOxim and SolGel1/1H invisible in an optical microscope at a magnification of 2000, which is only possible for surfaces that are smooth at nanoscale. We do not know the roughness of the SiPEG coatings. While we cannot determine roughness at molecular level, polymer chains like PDMS or PEG do not provide sharp steps as compared to crystalline materials.
- *High molecular mobility in the backbone and surface active chains* - Possibly in agreement for the surface active chains, but not for the backbone. PDMS with its low rotation barrier, possibly also PEG provide mobile surface chains. However, SolGel1H provides low adhesion with solely mobility in the surface active PDMS chains, but low mobility in the sol-gel backbone. SolGel1 without mobile chains at the surface, provides higher adhesion than SolGel1H.
- *A thickness which should be optimized with respect to the fracture mechanics of the interface* - We have no data on actual fracture mechanics. Whenever we tested almost identical coatings (Si/Si2, FR1/FR1thin) at different thicknesses, the thickness had no effect on adhesion.

For the applied epoxy adhesive, which might be more flexible than demanded for the applied adhesion model, no effect of coating thickness or flexibility/cross-linking of the coating backbone was detected, providing a possibility for fouling-release coatings which are thin enough to provide sufficient heat transfer for surface condensers. Those coatings providing an initial PBT adhesion below 0.4 MPa provided mobile chains at the surface. Besides the discussed model, the relevance of surface slippage based on the mobility of surface active chains has also been highlighted in studies removing ice instead of hard fouling from elastomeric surfaces [59,60].

3.5 Freshwater fouling in a heat exchanger simulating power plant conditions

Coated tubes and steel stripes were exposed to fresh water at 40°C at 1.6 m/s flow in two test runs applying water from the river Seine in Chatou, France. Run 1 applied 100% Seine water over 4 months. Fouling growth was monitored weekly for 3 months on one sample (three samples after 12 month) as fouling dry matter (DM) and total bacteria count (TBC), after 12 months as well as Legionella count (LP) (Figure 7, Figure 8, Table 3 and Table 4). The loop with the tubes coated with Si and SiPEG20/20i experienced limescale in week 9 due to a temporary malfunction of the automated sulfuric acid addition, affected results thereafter were discarded. Run 2 applied 7.5% Seine water dissolved in demineralized water to simulate cleaner water, leading to lower DM and TBC. LP was higher and for all samples above detection threshold of 75000 CFU. Fouling growth was monitored after 8 weeks on three specimens per coating. Within the precision of the method, Si and SiPEG20/20i did not perform significantly different to steel. In contrast to the bacteria

culture test, SiPEG20 did not reduce fouling in the freshwater exposure test. Coating FR2 reduced fouling in both bacteria culture and freshwater exposure test, showing less dry matter and bacteria count than steel. Fouling reduction of FR2 is in run 1 at detection threshold, while in run 2 with cleaner water, a significant reduction by a factor of about 10 was observed.

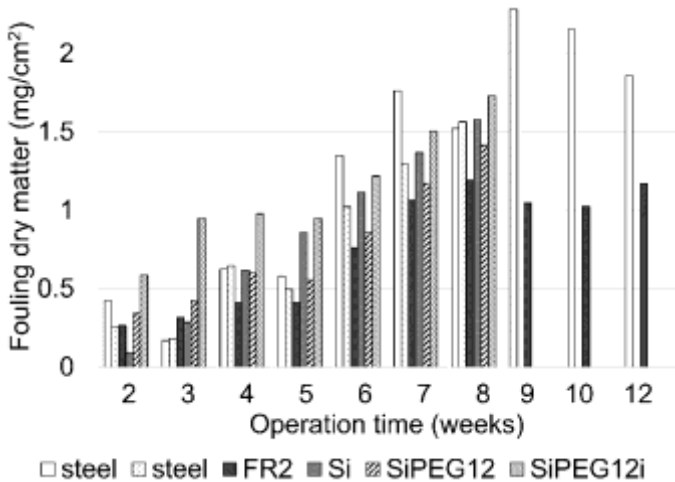


Figure 7: Fouling dry matter in run 1, exposure to water from river Seine

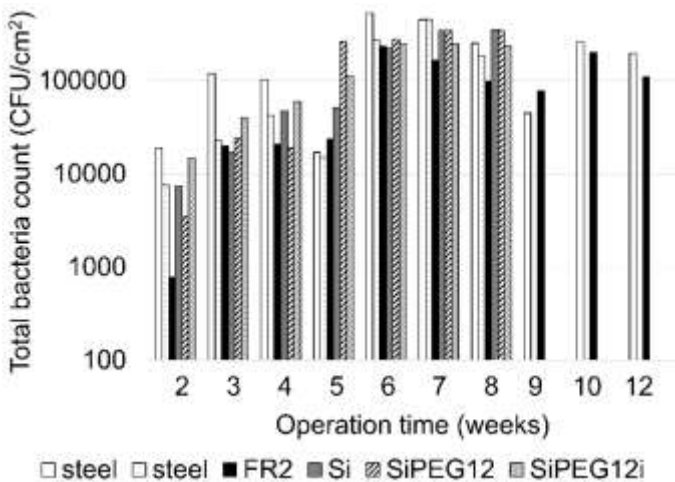


Figure 8: Total bacteria count in run 1, exposure to water from river Seine

Table 3: Fouling in run 1, exposure to water from the river Seine, after 12 weeks

Coating	DM (mg/cm²)	TBC (10 ⁵ CFU/cm²) / LP (10 ³ CFU/cm²)
steel	1.86±0.06	2.0±1.7 / 3.0±0.9
FR2	1.17±0.07	1.1±0.3 / 1.2±0.2

Table 4: Fouling in run 2, exposure to 7.5% river Seine water/92.5% demineralized water

Coating	DM (mg/cm ²)	TBC (10 ⁴ CFU/cm ²)
steel	0.44±0.10	1.9±1.0
FR2	0.044±0.004	0.13
Si	0.37±0.01	3.5
SiPEG20	0.30±0.02	2.2
SiPEG20i	0.57±0.02	0.59

In addition to fouling growth, fouling release was evaluated by cleaning metal stripes with a vertical water jet at different pressures. The stripes had been exposed to the same water, flow rate and temperature as the tubes of the fouling growth test, see Table 5 and Figure 9. While the lowest pressure readily removes the main portion of the fouling layer on all samples, the visual evaluation focused on a remaining continuous, thin fouling layer on the surfaces. For run 1, the stripes had been exposed for 4 months, Si and SiPEG20/20i were tested despite temporary limescale. For run 2, samples had been exposed for 8 weeks and the procedure had been modified by reducing the lowest pressure to 100 kPa and by increasing nozzle-surface distance from 10 to 20 mm to better differentiate coatings with low fouling adhesion.

Comparing fouling cleanability to the steel reference, the silicone rubber coating Si performed similar, while performance of SiPEG20/20i was inconsistent. Some specimen significantly facilitated fouling removal with complete removal at lowest pressure, while others did not. With solely two specimens per coating and test run, we can only speculate, that the present application of coatings SiPEG20 and 20i might lead to varying surface properties. Coating FR2 consistently showed easy fouling removal and, after run 2, demonstrated itself as the only tested surface with a partly fouling-free surface before cleaning.

Table 5: Presence of a continuous fouling layer after exposure in a freshwater loop at 1.6 m/s flow and after subsequent water jet cleaning applying different pressures

Surface	Run	Fouling layer (2: yes, 1: partly, 0: none)			
		after exposure	100/150 kPa jet	300 kPa jet	550 kPa jet
steel	1	2	2	1	1
	2	2	2	1	1
Si	1	2	2	2	1
	2	2	2	1	1
SiPEG20/20i	1	2	0 to 2	0	0
	2	2	0 to 2	0 to 2	0 to 2
FR 2	1	2	0	0	0
	2	1	0	0	0

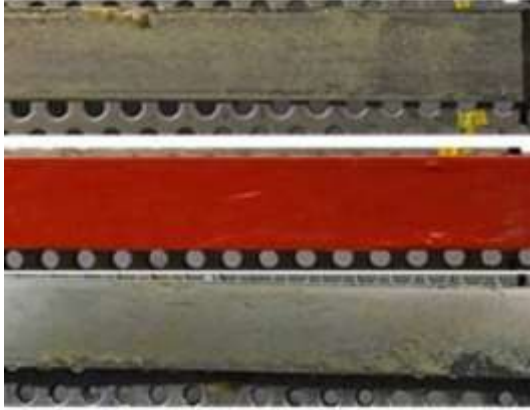


Figure 9: Steel stripes after freshwater exposure of run 2, before water jet cleaning. From top: steel, FR2, SiPEG20i

To evaluate coating integrity, the metal stripes of run 1 were evaluated for coating adhesion and contact angles. According to a cross-cut and tape test [61], adhesion of Si, SiPEG20, SiPEG20i and FR2 after freshwater exposure was good with a rating of 0. All coatings showed no visual degradation and were wiped with an ethanol-soaked tissue to remove any remaining fouling. Contact angle measurements as shown in Table 6 revealed that the surface properties have significantly changed, indicating either coating degradation or practically invisible scaling/fouling not removed by wiping. Silicone rubber Si became less hydrophobic, especially with respect to the receding contact angle, and the hydrophilic coatings SiPEG20 and FR2 became less hydrophilic with respect to advancing, receding, and for FR2 also static CA. Despite changed wetting behavior, FR2 still provided low fouling adhesion with respect to the water jet cleaning test.

Table 6: Shift of water contact angles. Initial values after exposure and water jet cleaning after subsequent wiping with an ethanol-soaked tissue

Coating	θ_{adv} (°)			θ_{static} (°)			θ_{rec} (°)		
Si	111	97±3	98±3	108	98±3	106±3	89	41±7	37±13
SiPEG12	81	108±3	113±5	110	113±4	114±6	0	34±15	52±4
FR2	75	105±2	105±2	66	106±3	106±2	0	54±10	52±4

4 Conclusion

Marine fouling release coatings are promising candidates to reduce fouling in surface condensers of thermal power plant. In our test, coating FR2 showed promising fouling reduction even at a total thickness for primer and topcoat of only 40-100 μm in a freshwater environment at a flow of only 1.6 m/s, thus outside its common specification range. However, this coating thickness is yet too high for applications in heat exchangers, significantly decreasing heat transfer.

Furthermore, coating performance would need to be demonstrated over several years instead of two to four months. For future development with respect to the cooling water circuit of power plants, it would make sense to evaluate also whether biocidal anti-fouling coatings provide

stronger fouling and bacteria reduction and whether these coatings are more environmentally friendly than adding a biocide to the cooling water.

Developmental coating SiPEG20i proved that a silicone coating providing a PEG-based hydrogel surface can be applied at a thickness around 10 μm including a primer to provide good adhesion to steel. Developmental coatings SiPEG20 and SiPEG20i, comprising 20% PEG, were selected by systematically varying PEG content. They are prepared from commercial precursors by a simple route via dispersing a PEG-PDMS-PEG triblock-copolymer in PDMS. Fouling growth in a bacteria culture test with *Pseudomonas aeruginosa* is reduced by more than a factor of 10 compared to PDMS without PEG or to steel, and fouling adhesion in a pseudo barnacle test by more than a factor of 10 compared to steel. Regarding freshwater exposure tests for 2-4 months, unlike the comparative, commercial coating FR2, SiPEG20/20i did not reduce fouling; however, fouling removal by water jet after exposure is facilitated.

Good performance in the applied laboratory tests, such as contact angle measurement, bacteria cultures and pseudo barnacle adhesion, does not guarantee low fouling growth or low fouling adhesion in real life. However, conversely, coating FR2, which showed promising real-life performance, did also perform well in the present laboratory tests. As real-life testing is costly and can be a developmental bottle neck, the laboratory tests may well be considered.

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Data availability

The raw/processed data required to reproduce these finding cannot be shared at this time due to technical or time limitations.

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