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INVITED FEATURE ARTICLE | February 4, 2020

Silicone-Based Fouling-Release Coatings for Marine Antifouling

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Abstract

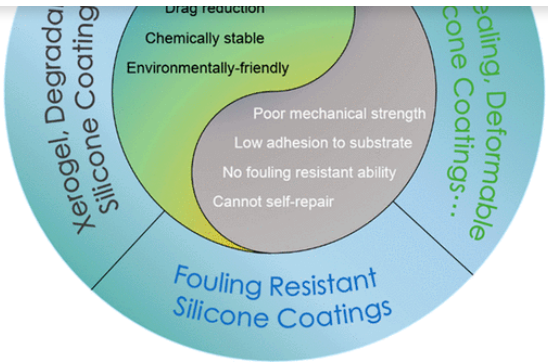
Marine biofouling profoundly influences marine industries and activities. It slows the speed and increases the fuel consumption of ships, corrodes offshore platforms, and blocks seawater pipelines. The most effective and economical antifouling approach uses coatings. Fouling-release coatings (FRCs) with low surface free energy and high elasticity weakly adhere to marine organisms, so they can be readily removed by the water shear force. FRCs

Langmuir

Cite this: *Langmuir* 2020, 36, 9, 2170–2183

https://doi.org/10.1021/acs.langmuir.9b03926

Published February 4, 2020



silicone-based FRCs have weak adhesion to substrates, low mechanical strength, and low fouling resistance, limiting their applications. In recent years, many attempts have been made to improve their mechanical properties and fouling resistance. This review deals with the progress in the construction of high-performance silicone-based fouling-release surfaces.

Subjects

Antifouling | Coating Materials | Elastomers | Silicones | Surface Interactions

Introduction

Marine biofouling is the unwanted accumulation of marine microorganisms, animals, and plants on surfaces immersed in seawater. It has detrimental effects on marine industries and facilities. (1−3) It slows the speed of ship hulls and increases their fuel consumption and greenhouse gas emissions. (4) Biofouling can also induce or promote the corrosion of metal or concrete structures, block the seawater pipelines of nuclear power plants, and hinder the nutrient exchange of aquaculture facilities. (5−7)

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Abstract

(8) The biocides should have high activity, low toxicity, and reasonable solubility in seawater, and only a few of them have found applications in antifouling coatings. The latter mainly consists of fouling-resistant coatings and fouling-release coatings (FRCs). Fouling-resistant coatings can prevent the adhesion of marine organisms. They are generally made of hydrophilic polymers such as those based on poly(ethylene glycol) (PEG) and zwitterions. (8) However, they are usually swollen in marine environments, leading to poor mechanical properties, which limits their applications. FRCs cannot inhibit the attachment of organisms, but the interfacial bond between organisms and the coating surface is weak due to their low surface free energy (SFE) so that the attached organisms can be readily removed by the water shear force coming from mechanical cleaning or the ship's navigation (Figure1). (9,10) Besides the low SFE, the low elastic modulus also plays an important role in FR performance. (11) A surface with a low elastic modulus can detach hard foulants such as barnacles. (12,13) Actually, the elasticity makes the surface deformable or dynamic, so the microorganisms find it difficult to land or settle on the surfaces. (14,15) This mechanism can be explained by the concept of dynamic surface antifouling (DSA). (16−21)

Figure 1

Figure 1. Schematic of fouling-release coatings.

Figure 1

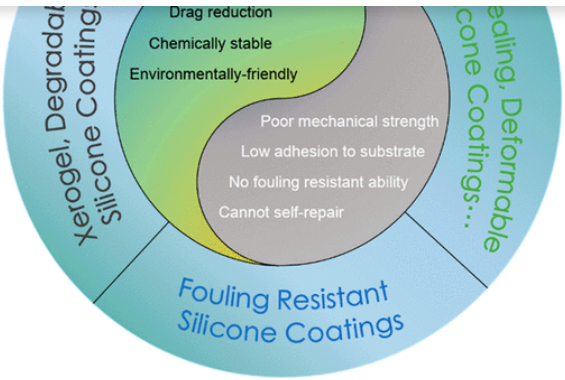

Figure 1

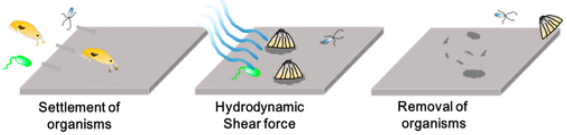

Figure 1. Schematic of fouling-release coatings.

occurs between a precursor of polysiloxane consisting of silanol end groups and a silicone cross-linker with many alkoxysilane groups. Apart from a low SFE and low elastic modulus, silicone elastomers also have low surface roughness (~1 μm), which is beneficial for reducing the frictional resistance during the navigation of ships. (22) Moreover, the cross-linking allows PDMS elastomers to be stable in marine environments.

Figure 2

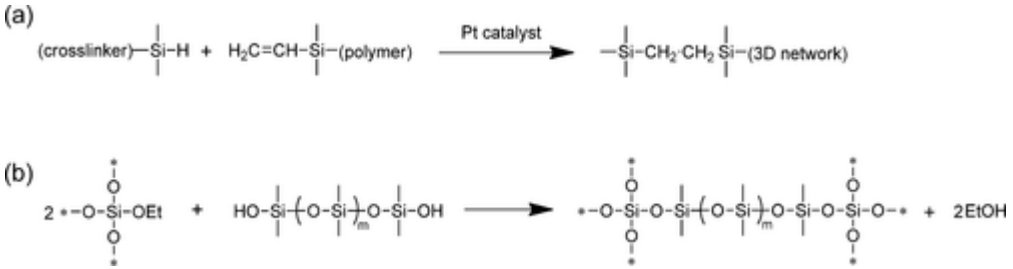

Figure 2. (a) Hydrosilylation reaction and (b) condensation reaction for the preparation of silicone elastomers.

Although silicone-based FRCs are ecofriendly with drag reduction and chemical stability, they have some drawbacks (Figure3). The low SFE is beneficial for FR performance but weakens the adhesion strength between the coating and the substrates. A tie coat is needed to enhance the adhesion in applications, which increases the costs and operating time. Moreover, silicone-based FRCs generally have poor mechanical properties and are susceptible to mechanical damage such as cutting, tearing, and puncturing, which reduces its service life. In particular, they have poor antifouling performance under static conditions, where they cannot prevent the growth of a slime layer consisting of diatoms and bacteria. (23−25) The diatoms can strongly adhere to silicone elastomers, and the accumulated slime cannot be released from ships even at high speeds (>30 knots). (23) In the past few years,

Figure 3

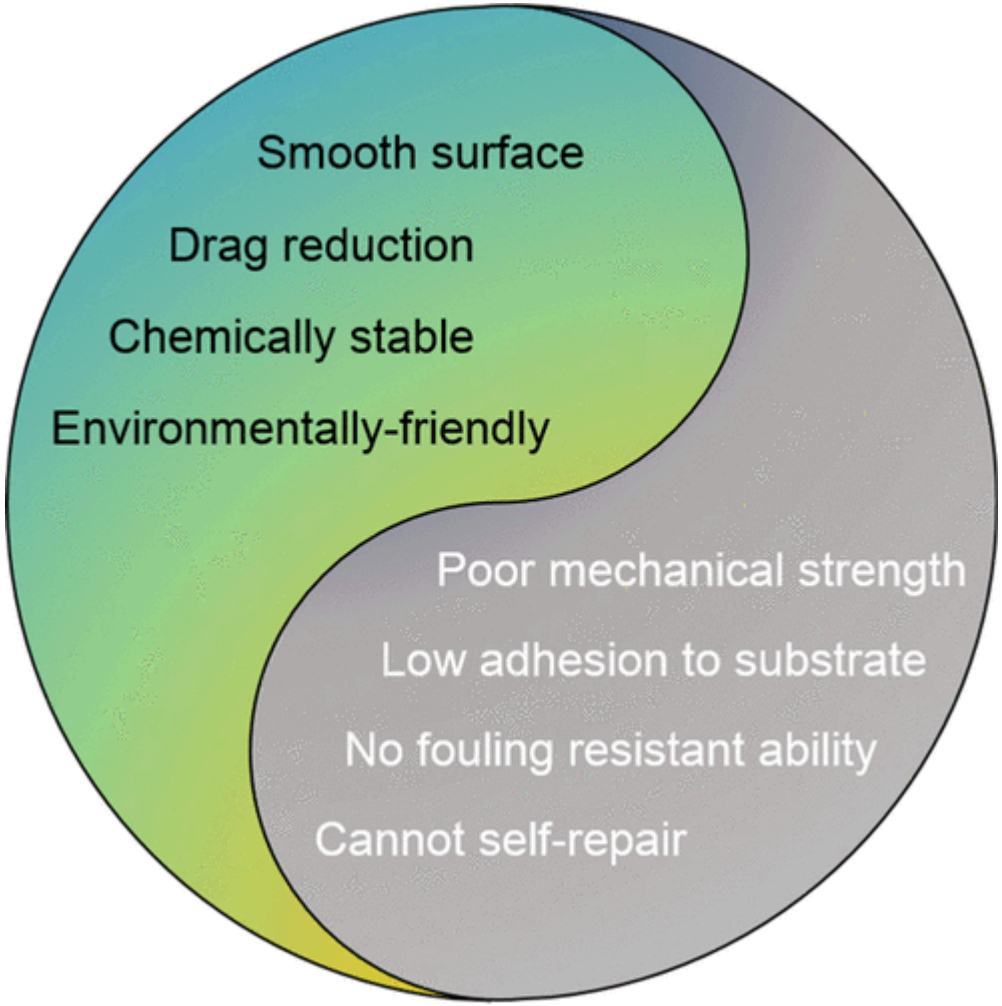

Figure 3. Advantages and drawbacks of silicone-based FRCs.

Modification of Conventional Silicone-Based FRCs

of the PDMS coating increased upon the addition of carbon nanotubes (CNTs). (26) El-Safty et al. prepared a ternary composite coating by incorporating incorporating graphene oxide (GO) sheet and alumina nanorod into silicone elastomers, and the flexibility and strength of the elastomers were increased. (27) They also incorporated titanium oxide (TiO_2) nanospheres into a PDMS matrix. The stiffness of the nanocomposites increased with the loadings. (28) The TiO_2-modified silicone coating could minimize the buildup of biofilms, prevent larval settlement, and kill macrofoulers when it was photoactivated. (29) Generally, only organisms in contact with the surface are subjected to the photocatalytic effect, thus reducing the risk to nontarget organisms. However, TiO_2 needs photoactivation by UV light and nonactivated TiO_2 had a limited effect on organisms, so such a coating is difficult to use in large-scale applications. (29)

Figure 4

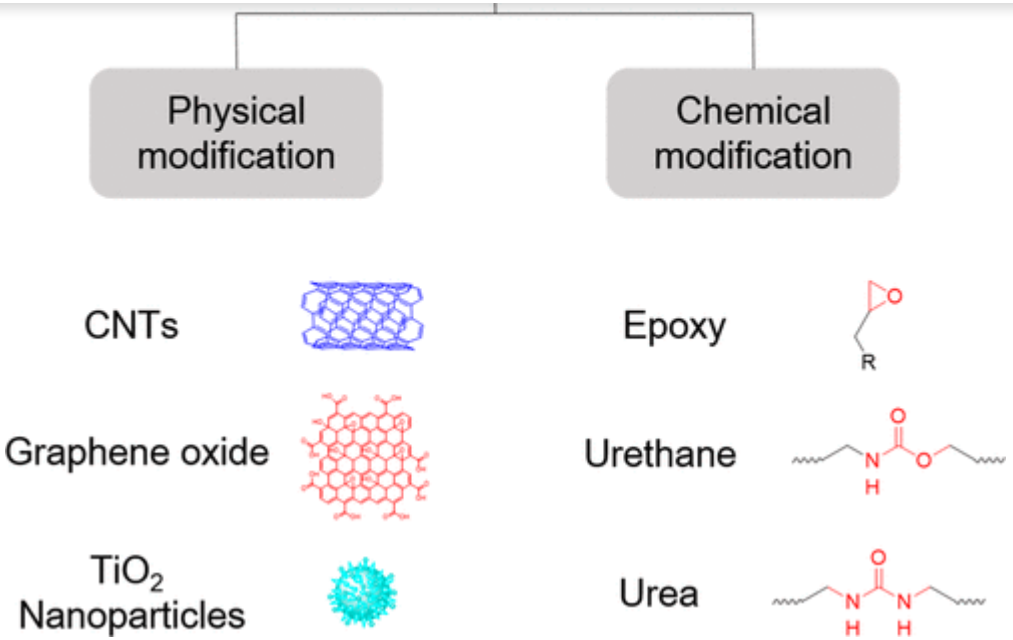

Figure 4. Approaches to improving the mechanical properties and adhesion strength of FRCs.

Adhesion Strength Improvement

The introduction of epoxy or urethane/urea groups into silicone can improve the mechanical strength and adhesion to a substrate (Figure4). Rath et al. synthesized an epoxy-modified silicone coating with isocyanate-capped PDMS and aliphatic epoxy resins, and the silicone–epoxy resins were cured with an amine hardener. (30,31) The bond pull strength of the coating with the primer was up to 2 MPa, which is enough to retain the integrity of the coating to withstand the release of fouling organisms, e.g., the removal of barnacles in shear mode. It also indicates the improvement in the adhesion strength.

substrate, and the residual isocyanate groups can react with hydroxyl groups in epoxy resin so that the adhesion strength is enhanced. The PDMS–polyurethane coatings have not only FR properties but also good adhesion.

The incorporation of urea groups into a silicone backbone can also enhance the mechanical and adhesion properties in that they can also form hydrogen bonds with the substrate. Liu et al. developed PDMS-based polyurea with PDMS soft segments and 1,6-hexanediamine hard segments. (38) The coating had an adhesion strength of up to 2 MPa, much higher than that of the commercial PDMS Sylgard 184 (~0.4 MPa). Thus, the coating retained its integrity in the dynamic marine field test and exhibited a nonfouled surface after three test cycles. In contrast, the PDMS control completely detached from the substrate and exhibited poor antifouling performance. Moreover, the removal of the fouling organism (diatoms *N. incerta*) under water jet pressure (20 kPa) revealed that the coating had FR performance similar to that of an unmodified PDMS coating. In the static field test, the coating was much less fouled than the control panels in the South China Sea for 60 days. Note that although the approaches mentioned above can strengthen the mechanical properties of silicone-based FRCs effectively, they also reduce their elasticity and cannot improve the fouling resistance due to the lack of active fouling-resistant moieties.

Fouling Resistance Improvement

To improve the fouling resistance of silicone-based FRCs under static conditions, amphiphiles, zwitterions, quaternary ammonium salts (QASs), and antifoulants have been introduced. PEG-based amphiphiles have resistance to protein and cell adhesion due to their hydration layer and steric excluded volume effects. (39) Some attempts have been made to use them in marine antifouling coatings. (40−48) International Paint developed the FRCs Intersleek 1100SR in 2013. It showed good release performance with respect to barnacle (*B. amphitrite*) cyprids and diatoms (*N. incerta*). (49,50) Olsen et al. prepared the coating by

PDMS block and a PEGylated fluoroalkyl-modified polystyrene block to a PDMS matrix. The coating had hydrophobic and lipophobic properties independent of the copolymer composition and content because of the chemical incompatibility between the copolymer and PDMS. The bioassays displayed that the modified coating had a higher removal rate of *Ulva* sporelings than did the PDMS control. (54) Ober et al. investigated the effects of the polymer backbone, side-chain structures, and monomer sequence on the antifouling and fouling-release performance of PDMS-based and PEO-based block copolymer coatings functionalized with an amphiphilic oligopeptide and oligopeptoid. (60,61) Their fouling-release performances were mainly determined by the polymer backbone, and peptoid-functionalized coatings outperformed the peptide-functionalized coatings because the former do not have hydrogen bond donors. They also prepared an antifouling film by dispersing amphiphilic triblock copolymers in a cross-linked PDMS network (Figure5b). (62) The film displayed evident FR performance against *U. linza* even at low block copolymer loadings (1 and 4 wt %), and the diatoms were also easily removed from the surface. The amphiphiles are able to migrate to the surface driven by the low SFE fluorinated segments during film formation, achieving excellent fouling resistance or FR performance. However, those amphiphiles are simply anchored to the surface by physical interactions. They leach out continuously, and the fouling-resistant efficiency dramatically decreases once the amphiphiles are completely released. Moreover, the impact of the leachate on the environment is uncertain.

Figure 5

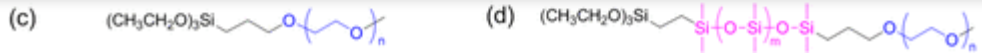

Figure 5. (a) PDMS-PEG-based amphiphiles. (b) Amphiphilic block copolymers. (c) PEO control. (d) PEO-silane amphiphiles.

Grunlan et al. chemically cross-linked poly(ethylene oxide) (PEO)/PEO-silane amphiphiles with PDMS and investigated the effects of the PEO length (*n*, number of EO units) and siloxane tether length (*m*, number of siloxane units) on the fouling resistance (Figure5c,d). (63−66) When $n = 8$ or 16 and $m \geq 4$, the coating had the highest resistance to protein adsorption as well as to microbial biofilm growth. This is because the hydrophobic nature and flexibility of the siloxane tether allow them and the attached PEO segment to move through the PDMS network, thus reducing protein adsorption. However, the PEO-modified silicone control ($m = 0$) did not show higher resistance than the unmodified silicone. The PEO control without a siloxane tether may be embedded in the bulk instead of migrating to the surface. The PDMS network was also modified by grafting trimethoxy-terminated PEG (TMS-PEG) and silanol-terminated PDMS with trifluoropropyl pendent groups (CF_3-PDMS). The coating containing both TMS-PEG and CF_3-PDMS showed enhanced FR properties. The incorporation of only TMS-PEG into PDMS slightly improved the fouling resistance since PEG had a higher SFE than did PDMS and was migrated with difficulty to the surface. (67)

Considering that the amphiphiles may be trapped in the bulk of silicone coatings, leading to swelling and poor antifouling efficiency, Zeng et al. developed surface-enriched and nonleaching amphiphiles via the telomerization of dodecafluoroheptyl methacrylate (DFMA), poly(ethylene glycol) methyl ether methacrylate (PEGMA), and 3-mercaptopropyl trimethoxysilane (KH590). (68) The amphiphiles with trimethoxy groups were chemically attached to a silicone elastomer by a condensation reaction (Figure6a). The fluorinated telomer incompatible with silicone had low surface energy, so it tended to migrate onto the

the coating could inhibit the adhesion of marine bacteria *Pseudomonaus* sp., and almost no bacteria were observed on the coating surface (Figure6c). The coating was also able to prevent the formation of bacterial biofilms and the adhesion of diatom *N. incerta*.

Figure 6

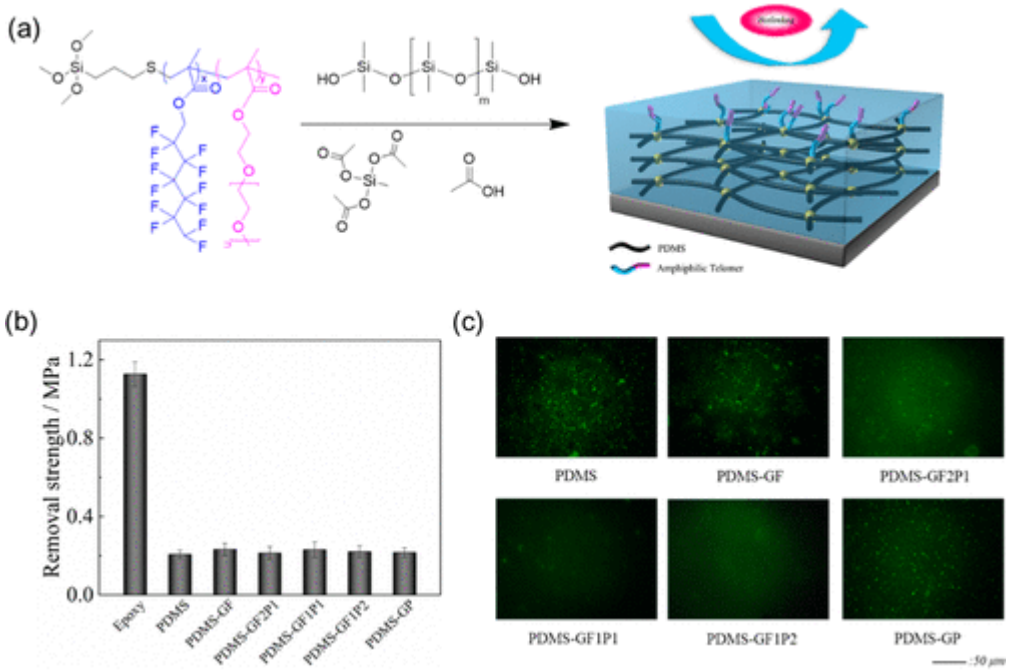

Figure 6. (a) Preparation of PDMS-based coating. (b) Removal strength of adhered pseudobarnacles from the coating. (c) Fluorescence microscopy images of bacteria adhered to the coating. Reproduced from ref (68). Copyright 2019 American Chemical Society.

Besides PEG-based amphiphiles, zwitterionic polymers can also form a hydration layer via electrostatic interactions with water, which can effectively prevent protein adsorption and be

pacifica and diatom *N. incerta*. Lopez et al. prepared a zwitterionic surface by grafting PSBMA chains onto a PDMS elastomer. (73) The surface had resistance to bacteria *C. marina* and barnacle cyprid *A. amphitrite* as well as easy removal for biofilm retention properties. Since zwitterionic polymers have poor compatibility with silicone, they are usually introduced by surface grafting and so are difficult to use in large-scale applications.

Figure 7

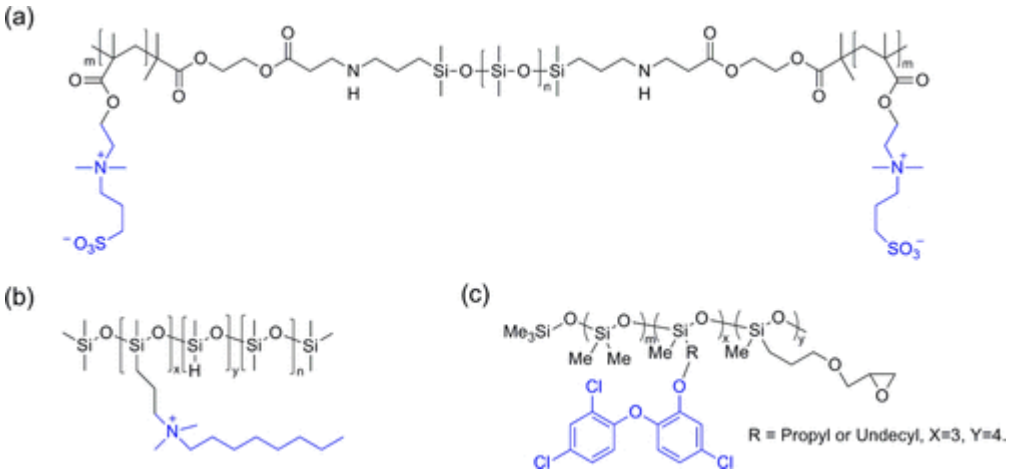

Figure 7. (a) PSBMA-*b*-PDMS-*b*-PSBMA triblock copolymer. (b) Grafting QAS groups on a siloxane backbone. (c) Grafting TCS on a PDMS backbone.

Quaternary ammonium salts with long carbon alkyl chains (number of carbon atoms >8) have proven effective in inhibiting biofouling with a contact-killing mechanism. (74−76) Microorganisms can adhere to surfaces functionalized with QAS by electrostatic interactions. However, the long alkyl chains of QAS would kill them by penetrating their cell membranes. (77) Chisholm et al. prepared QAS-modified PDMS by a two-step procedure in

high cross-linking density showed a high biocidal activity without leachate toxicity and good stability because it had low swelling. The coating reduced 80% biofilm retention of *C. lytica* and 90% biofilm growth of *N. incerta*. They also studied the effects of QAS alkyl chain length, QAS concentration, and molecular weight of the silanol-terminated PDMS on fouling resistance and release properties. (79,80) The coating with 18-carbon alkyl chain showed the best antifouling and fouling-release performance. The surface structures of the PDMS with QAS moieties in air, water and in a nutrient growth medium at molecular level were characterized by the sum frequency generation vibration spectroscopy. (81,82) It revealed that QAS was segregated to the coating surface, and the surface structure was profoundly influenced by the length of alkyl chain attached to the nitrogen atom as well as the length of alkyl chain between the nitrogen atom and the silicon atom.

Although the amphiphiles, zwitterionic polymers, and QAS can enhance the fouling resistance of silicone-based FRCs, they are often swollen due to the presence of hydrophilic moieties, significantly reducing their stability and mechanical properties. As discussed above, the silicone with self-enriched amphiphiles on the surface developed by Zeng et al. can reduce the swelling since the hydrophilic segments can migrate to the surface of coatings. (68) Similarly, Webster et al. developed a self-stratified polyurethane-polysiloxane coating. (83,84) The work may also provide an approach to solving the swelling problems. In particular, grafting a hydrophobic antifoulant onto silicone can effectively suppress the swelling. Thomas et al. covalently grafted antifoulant triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) (TCS) (Figure7c), a broad spectrum antimicrobial agent, to the siloxane backbone via a hydrosilylation reaction. (85) The silicone resins were cured by using vinyl-terminated PDMS for hydrosilylation and 1,3-cyclohexane-bis(methylamine) for epoxy cross-linking. The coating had a hydrophobic surface (WCA > 90°) and a low SFE (<30 mJ m^{-2}). It had moduli in the range of 0.1–10 MPa and good antifouling performance in static seawater immersion. However, the antifoulant may be embedded in bulk PDMS

coating exhibited better FR performance than pristine PDMS even with an antifoulant content of less than 0.6 wt %. Moreover, the coating had an excellent antibiofilm property against *Pseudoalteromonas tunicate* with about 100% adhesion reduction.

Xie et al. prepared a PDMS-based polyurethane coating with chemically attached antifoulant *N*-(2,4,6-trichlorophenyl) maleimide (TCM) via a thiol–ene click reaction. (87) The presence of TCM slightly changed the SFE but remarkably improved the fouling resistance. The coating with a high content of TCM can effectively inhibit the adhesion of marine bacteria (*M. luteus*), diatoms (*Navicula*), and barnacle cyprids in laboratory bioassays. The 4-month marine field test in the South China Sea demonstrated that the coating had a good antifouling ability. Besides, the coating had higher adhesion to a substrate (>1.0 MPa) and a higher modulus than the PDMS elastomer owing to the hydrogen bonding.

The antifoulants are often embedded in the bulk of the coating containing PDMS because of its low SFE. As a result, a large quantity of antifoulants had to be added to achieve the desired fouling-resistant performance. In turn, this would increase the SFE and elastic modulus of silicone. (85) To reduce the antifoulants used, Xie et al. prepared a self-stratifying silicone coating by cross-linking a telomer consisting of TCS and DFMA with bis-silanol-terminated PDMS (Figure8a). (88) The low SFE fluorinated segments connected to the antifoulants would migrate onto the surface during film formation due to their incompatibility with PDMS, forming an antifoulant-enriched surface. The self-stratifying property of the coating was examined by XPS, and the nonleaching of the grafted antifoulant was confirmed by a leachate toxicity test. The leachate from the coating did not have an effect on diatom growth (Figure8b). The coating surface remained hydrophobic in artificial seawater immersion for 90 days. The coating had a removal strength of adhered pseudobarnacles close to that of PDMS (Figure8c). In particular, it exhibited excellent resistance to the growth of a marine bacterial biofilm (*Pseudomonas* sp.) and the adhesion of diatoms (*N. incerta*). The 3D real-time motion behavior of marine bacteria *Pseudomonas*

the fouling-resistant groups can be linked with fluorinated groups to realize the self-stratification.

Figure 8

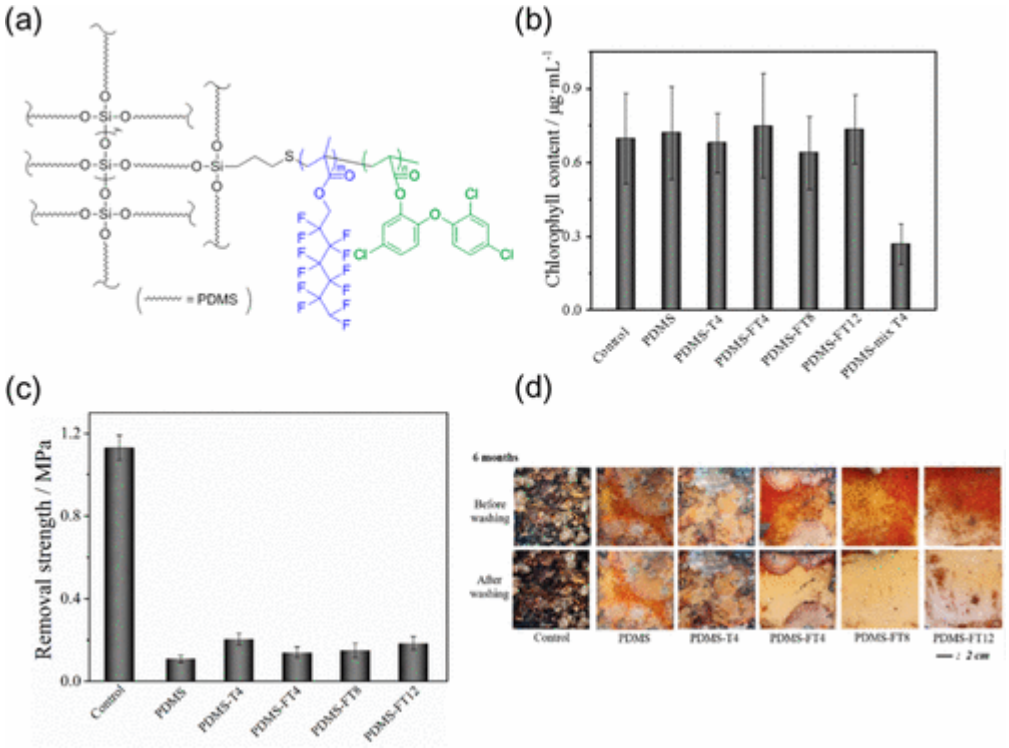

Figure 8. (a) Structure of a cross-linked PDMS coating with telomers. (b) Effect of leachate toxicity on diatom growth. (c) Removal strength of adhered pesudobarnacles from the coating. (d) Marine field test of coating immersed for 6 months. Reproduced with permission from ref (88). Copyright 2019 John Wiley & Sons.

Biomimetic Fouling-Release Surface

ability to inhibit fouling. Mimicking the behavior of mucus secreted by organisms such as pitcher plants and fish, silicone oil and other fluids were added to the silicone-based FRCs. The silicone oil can migrate to the interface between coatings, forming a weak surface layer which is beneficial for detaching the biofouling. (8) Actually, the fluids form a dynamic and unstable surface which makes it difficult for the microorganisms to land and grow. (20) In 1977, Milne incorporated silicone oil into cured silicone rubber to improve the AF efficiency. (89) Cella et al. studied the FR performance of silicone coatings with incorporated silicone oil. (90) The RTV11 PDMS elastomers amended with 10 wt % polydimethyldiphenylsilicone oil could effectively reduce the adhesion of barnacles, oysters, and tubeworms. The silicone oil formed a mobile surface layer that could reduce the coefficient of friction and favor an easier release of fouling organisms. (91) However, the system had limited improvement in releasing the adherent slimes and soft fouling organisms. Webster et al. investigated the FR performance of a siloxane-polyurethane coating with infused silicone oil. (92) The laboratory biological assays demonstrated that the coating had good FR performance toward macroalga (*U. linza*), barnacles (*A. amphitrite*), and marine mussels (*G. demissa*), yet the coating also had little effect on releasing diatoms (*N. incerta*) and bacteria (*C. lytica*). Howell et al. developed a self-replenishing vascularized FR surface made by molding or embedding 3D vascular systems into PDMS and filled them with silicone oil (Figure9a). (93) Biofouling tests showed that the lubricant-infused PDMS could reduce bacteria and the green microalga biofilm adhesion (Figure9b). Moreover, the 3D vascular PDMS systems can replenish silicone oil from an outside source. To understand the mechanism underlying the adhesion prevention of slippery silicone coatings, Amini et al. prepared a lubricant-infused coating by infusing silicone oil into a cross-liked PDMS network (**i**-PDMS). (94) It had low mussel (*Perna viridis*) attachment and ultralow adhesive strength under controlled laboratory conditions (Figure9c) as well as good antifouling performance for 16 weeks in marine field studies (Figure9d). They explained that the lubricant infusion would deceive the

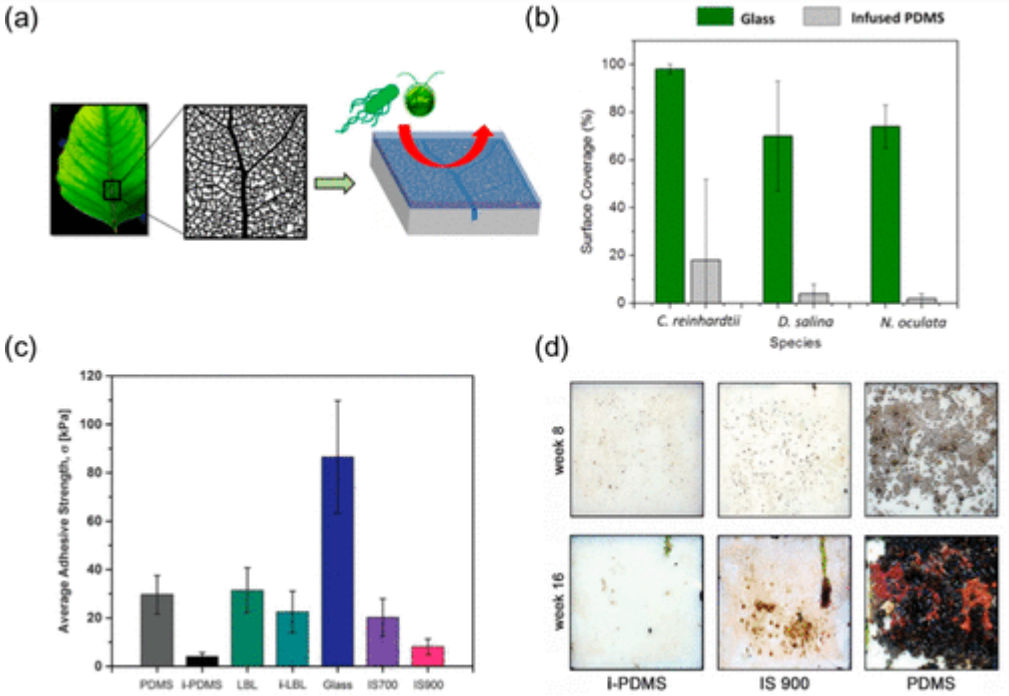

Figure 9. (a) Self-replenishing vascularized system. (b) Bacterial biofilm contamination of the lubricant-infused PDMS and glass. (c) Average adhesive strength of mussels on different surfaces. (d) Images of each surface after 8 and 16 weeks of static immersion. (a and b) Reproduced from ref (93). Copyright 2014 American Chemical Society. (c and d) Reproduced with permission from ref (94). Copyright 2017 American Association for the Advancement of Science.

Note that although the addition of silicone oil improves the FR ability of silicone coatings, it may lower the mechanical properties. When the silicone oil is depleted, the coatings become more brittle so that they are easily damaged. (95) Besides, the effect of the released oil on

Deformable Silicone Coatings

Inspired by a biological surface with self-cleaning ability by deformation and motion, Zhao et al. fabricated a silicone elastomer surface with deformable topography in response to external stimuli. (99,100) The external electric field can deform the polymer surface, and the adherent biofilms (*Cobetia marina*) can be detached actively and effectively. The removal of the biofilm increased with the strain of surface deformation. The deformation of the polymer also significantly reduced the shear force required for barnacle detachment. The controlled deformation of silicone elastomers via pneumatic actuation was also examined to understand the release of biofilm under laboratory and field tests. (100) The controlled deformation of the elastomeric substrate detached the formed biofilms in the laboratory assays or in the marine environment. Actually, the deformation leads to a dynamic surface on which the microorganisms cannot land or adhere. (20)

Tian et al. prepared graphene-silicone elastomer (GSE) composite materials with a movable tentacle structure (TS-GSE) by imitating the surface of soft coral. (101) The coating had an adjustable elastic modulus, low SFE, and strong electronegativity. It exhibited good antiadhesion performance against the Gram-negative and Gram-positive bacteria under both static conditions and dynamic conditions. Computational fluid dynamics simulation analysis revealed that the GSE film generated regular harmonic motion through deformation, which drives the bacteria away from the surface. However, its long-term durability and persistence need to be tested in the future.

Self-Healing Silicone Coatings

As mimicry of natural organisms, self-healing polymers have been prepared for coatings, wearable devices, and soft robots in recent years. (102) The self-healing is expected to

attributed to high-density hydrogen bonds in polyurea. As shown in Figure10b, the cut elastomer was able to recover in 48 h at room temperature in either air or seawater. The self-healing efficiency was more than 90% determined by ultimate strength from the tensile test. The introduction of organic antifoulant 4,5-dichloro-2-*n*-octyl-4-isothiazoline-3-one (DCOIT) can further improve the self-healing efficiency. It reached 100% with 10 wt % DCOIT. This is understandable. The polyurea chains become more flexible when they mix with DCOIT acting as a plasticizer, so the self-healing efficiency increases. Besides, the PDMS-polyurea coating had an adhesion strength above 1 MPa, depending on DCOIT content (Figure10c). The polymer can control the release of DCOIT at a constant but low rate. This is because the hydrophobicity of DCOIT and its chemical affinity for the urea groups cause it to remain in the polymer matrix, but it can migrate to the surface by osmotic pressure and dissolve into seawater gradually. As a result, the coating exhibited excellent antifouling performance after static immersion in seawater for 180 days (Figure10d). To the best of our knowledge, this is the first report on self-healing marine antifouling coatings. Other self-healing systems based on metal–ligand coordination (104) or the boronic ester bond (105) may also be used to prepare marine antifouling coatings.

Figure 10

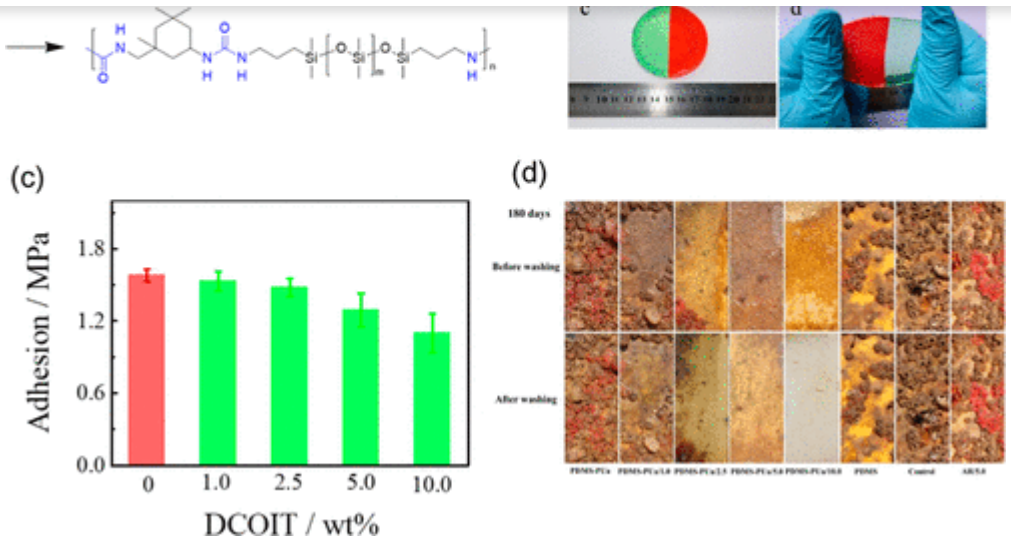

Figure 10. (a) Synthesis of PDMS-based polyurea. (b) Images of the self-healing process of damaged films. (c) Adhesion strength of the coating with different contents of antifoulant. (d) Coating after immersion in seawater for 180 days. Reproduced with permission from ref (103) . Copyright 2017 Royal Society of Chemistry.

Other Fouling-Release Surfaces

Xerogel Silicone Coatings

Sol–gel-processed xerogel silicone coatings with tunable surface characteristics are environmentally friendly with low cost. They also can be prepared under ambient conditions. (106) A variety of procedures such as spraying, brushing, dip coating, and spin coating can be used to prepare xerogel films with uniform, uncracked, and smooth surfaces. (106) The sol–gel xerogel is potentially used as environmentally benign FRCs.

ratio of 1/1 had good FR to fouling organisms *Ulva* sporelings, *B. amphitrite* cypris larvae, and juvenile barnacles. (107,113) Moreover, the xerogel coating had a smooth surface with roughness in the range of 0.1–1 nm, which can significantly decrease the settlement and increase the removal rate of fouling organisms. (114) However, the coating had limited efficiency to diatom stains. The introduction of *n*-octadecyltrimethoxysilane (C18) into the C8/TEOS xerogel in a suitable ratio could improve the FR performance to sporelings *Ulva* and diatoms *Navicula*. (109)

The xerogel coatings have limited fouling resistance due to the lack of active antifouling moieties. Chen et al. incorporated a novel amphiphilic reactive fluorocarbon acrylate-PEG oligomer (FP) by the telomerization of DFMA, PEGMA, and 3-mercaptopropyl triethoxysilane (KH580) into a hybrid coating by a facile sol–gel procedure (Figure11a,b). (115) The coating had a high transmittance (>99%) in the range of 400 to 800 nm. It had adhesion to an epoxy substrate higher than PDMS (Figure11c). The coating also had low SFE (17–24 mJ m^{-2}) and low surface roughness (R_q < 2.8 nm), so it had a removal strength of adhered pesudobarnacles lower than that of the PDMS control. Moreover, the coating had much higher hardness than the PDMS control. The bioassays demonstrated that the coating could effectively resist *Pseudomonas* sp. and its biofilm as well as diatoms *N. incerta* (Figure11d). This organic–inorganic xerogel coating combines the advantages of a silicone elastomer and the robustness of an inorganic component. They have not only good FR performance but also mechanical properties.

Figure 11

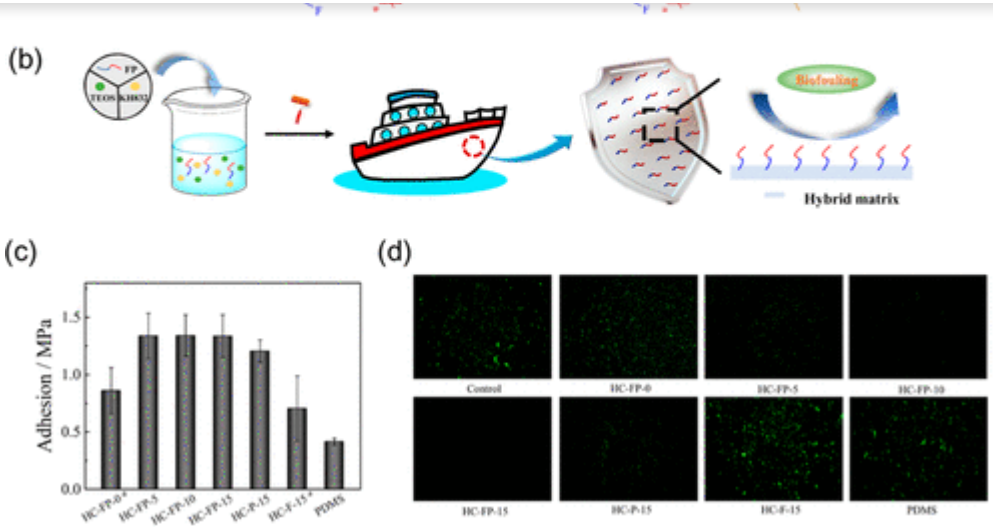

Figure 11. (a) Synthesis of the telomer. (b) Preparation of the hybrid coating by a sol–gel procedure. (c) Adhesion strength of the hybrid coating. (d) Fluorescence microscopy images of *Pseudomonas* sp. adhered to the hybrid coating. Reproduced with permission from ref (115). Copyright 2020 Royal Society of Chemistry.

Degradable Silicone Coatings

A degradable polymer coating can form a dynamic surface so that the marine biofouling even under static conditions can be inhibited. (20) Degradable silicone is expected to have surface renewal to FRCs and thus improve the static antifouling property. Bressy et al. prepared a new silicone coating that combined the silicone elastomers with a hydrolyzable polyester by a condensation reaction between bis-silanol PDMS and bis(trialkoxysilane)-terminated polyester macro-cross-linkers. (116) Poly(ε-caprolactone) (PCL), poly(D,L-lactide-*co*-glycolide) (PLGA), and poly(ε-caprolactone)-*b*-PDMS-*b*-poly(ε-caprolactone) (PCL-PDMS-PCL) were used as hydrolyzable components. Each coating had a low SFE which is

Moreover, the coating may be considered to be an ambiguous surface in that it displayed significant chemistry renewal with contact angle hysteresis $\Delta\theta \geq 40°$. They prepared another degradable silicone coating by the physical mixing of PCL, PCL-PDSM-PCL triblock copolymer, and poly(bis(trimethylsilyloxy)methylsilyl methacrylate) with a PDMS matrix. (117) It exhibited antiadhesive performance to barnacles *A. amphitrite* with only 15 wt % hydrolyzable polymer content and a longer antifouling efficacy than the pristine PDMS after immersion in the Mediterranean Sea. Note that the degraded segments of these polymers contain polysiloxane. Its influence on the marine environment needs to be assessed in the future.

Conclusions and Perspectives

Silicone-based FRCs are environmentally friendly and chemically stable with drag reduction properties. However, their poor mechanical strength, low adhesion strength to substrates, and low fouling resistance limit their applications. The addition of nanofillers or chemical modification with epoxy and urethane can improve the tensile or adhesion strength of FRCs, but it usually reduces its elasticity and hence the fouling-release ability. The addition of fluids such as amphiphiles or silicone oil can improve their fouling resistance but may reduce the mechanical strength. The functionalization of FRCs with zwitterions, quaternary ammonium salts, and antifoulants can effectively improve their fouling resistance but make them swell in marine environments or increase their elastic moduli. The surface-enriched, nonleaching strategy may be a good way to optimize the FR performance and mechanical properties of silicone-based FRCs. Self-healing FRCs can even work upon damage, but their mechanical properties are often not high enough. The organic–inorganic hybrid functional silicone is the combination of silicone elastomer and inorganic particles with antifouling groups. They can have good FR performance and mechanical properties at the same time, and they may represent the new generation of FRCs.

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Notes

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Biographies