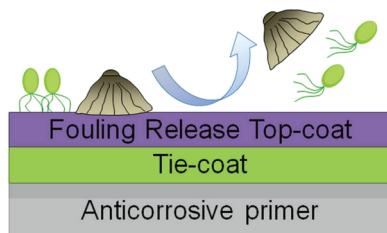


Fouling Release Coatings: A Nontoxic Alternative to Biocidal Antifouling Coatings

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1. INTRODUCTION

Any surface immersed in seawater is subjected to the settlement of marine organisms (bacteria, algae, mollusks), known as fouling or biofouling. This unwanted colonization has serious impacts, in particular for the naval industry, with deterioration of the surfaces, increased roughness, increased fuel consumption, and loss of maneuverability of the vessels. Marine species may also be introduced into non-native environments through ship transport. Marine biofouling is a worldwide problem, costing billions of dollars per year in transportation.^{1,2} Antifouling (AF) coatings have been developed to prevent the settlement of fouling organisms. The earliest techniques proposed were pitch, tar, wax, heavy metals (lead), or toxic (arsenic-based) coatings.³ In the mid-1960s, self-polishing AF paints incorporating tributyl tin (TBT-based compounds) were the first to show durable efficiency with a modest cost of production. TBT acts as a broad-spectrum biocide and can be incorporated into paints in such that it is released from the coating and effectively inhibits fouling on a ship hull up to five years. However, in the late 1970s, the effects of TBT became apparent. Several studies indicated that TBT-based compounds had adverse effects on aquatic life and more specifically on nontargeted fouling organisms such as oysters, due to its high persistence and toxicity.^{4,5} The impact of TBT on marine organisms induced many governments to restrict its use. France was the first to ban the application of TBT-based AF paints on ships less than 25 m long in 1982.⁶ In October 2001, the International Maritime Organization took into account the adverse effects of TBT on the marine environment. An order was issued banning the use of this type of biocide in the manufacturing of AF paints from first January 2003 and the presence of these paints on ship surfaces from first January 2008.⁷ The restriction on the use of TBT led to a renewed use of copper-based paints and/or the use of new paints incorporating high levels of copper. However, copper (and other metals) may also pose problems for the environment.⁸

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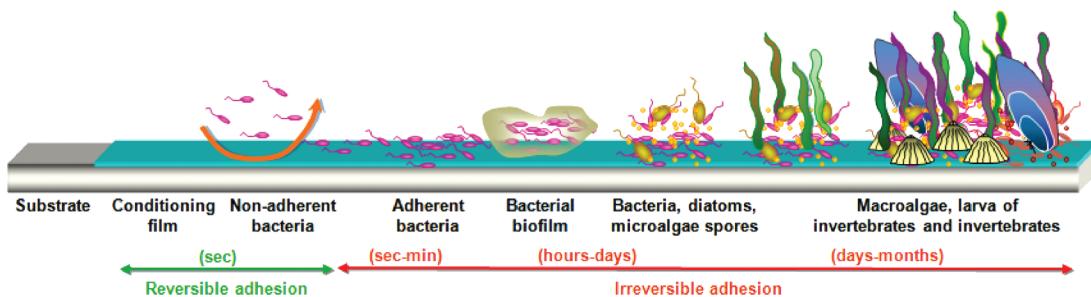


Figure 1. Development processes of marine fouling. Adapted with permission from ref 12. Copyright 2005 EDP Sciences.

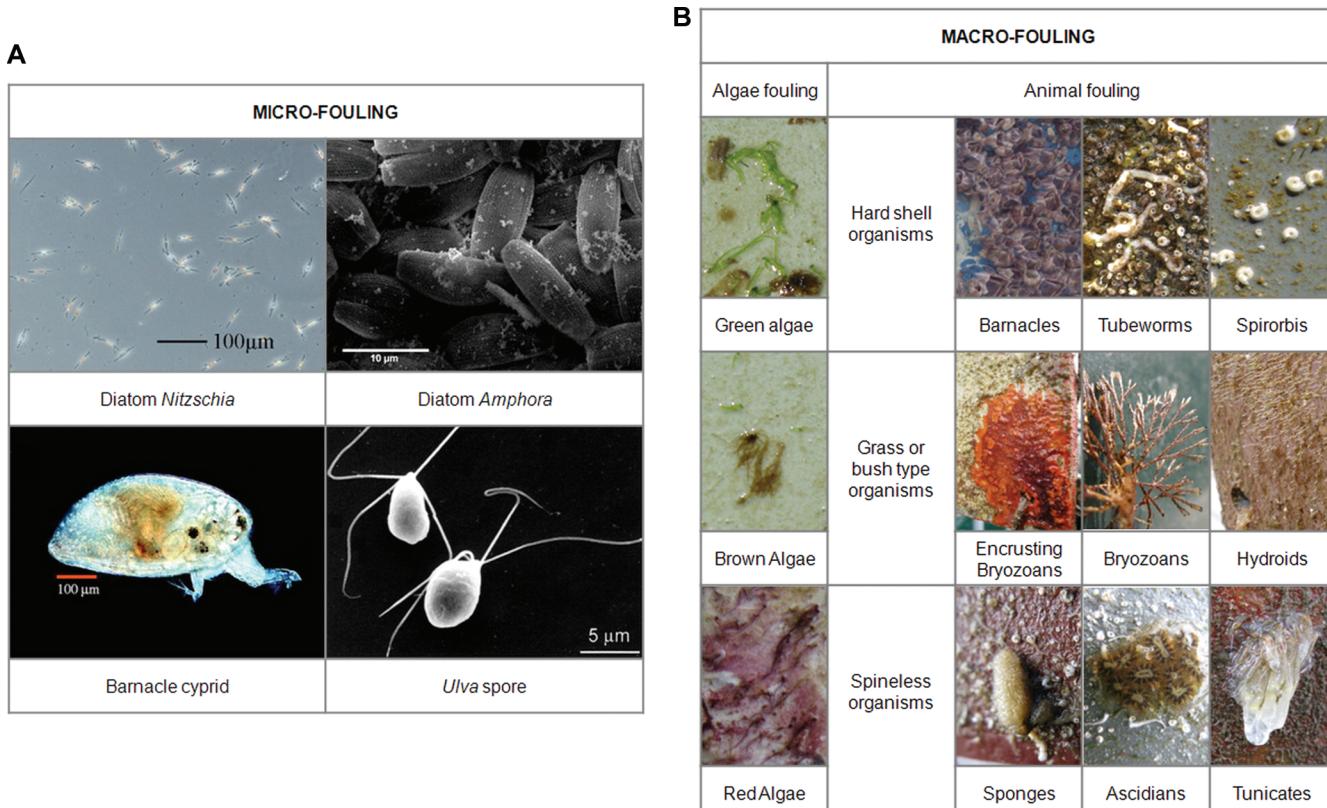


Figure 2. (A) Marine micro-organisms currently settled on pristine man-made surfaces immersed in natural seawater. (B) Marine macro-organisms currently settled on pristine man-made surfaces immersed in natural seawater. *Diatom Nitzschia*. Reprinted from ref 15. Copyright 2010, with permission from Elsevier. Barnacle cyprid. Reprinted with permission from ref 16. Copyright 2008 The Royal Society. *Ulva* spore. Reprinted with kind permission from ref 17. Copyright 1999 Springer Science & Business Media.

Along with the increasing use of copper in AF paints, several alternatives to TBT have been developed, such as the use of synthetic and natural biocides.⁶ However, the global costs of development of new biocides or new AF coatings incorporating biocides have increased, as they are now subject to restrictive legislations (e.g., the European Biocidal Products Directive, which requires several risk studies before registration and marketing authorization).⁷ These increased costs associated with the use of biocides and the anticipation of future prohibitions reactivated the development of nontoxic approaches, particularly low-surface-energy Fouling Release Coatings (FRCs), research into which was sidelined by the success of TBT-based AF coatings in the 1970s. Omae⁹ and Yebra et al.¹⁰ mentioned that FRCs including silicone and fluorine-based coatings may be an answer to the pressing need for AF solutions, as well as the need for the development of alternatives to chemically active coatings and more environ-

mentally friendly AF strategies. Other alternatives are also considered, including enzyme-based coatings and microtopographical surfaces. This review is an overview of the current technologies developed for use as AF coatings and deals particularly with the progress made in FRCs from the end of the 1990s. After a description of marine fouling colonization and its key impacts on immersed surfaces, the main developments in the domain of biocidal and nontoxic AF coatings are reported. The FRC approach is considered in more detail. The different parameters influencing initial bioadhesion and fouling release (FR) ability on such coatings are discussed. Then the chemical structure and the main characteristics of silicone- and fluorine-based polymers, the two major polymeric materials exhibiting FR properties, are presented. Moreover, the impact of coating formulation on the FR performances is also discussed. Finally the latest developments in FRCs are

mentioned, particularly hybrid systems that improve original FR properties by combination with other materials.

2. MARINE FOULING

2.1. Process of Colonization

2.1.1. Key Steps of Marine Fouling Growth. The immersion in seawater of a biologically nontoxic material leads to surface colonization by thousands of marine organisms that strive to complete their life-cycle. The process of biological fouling is often grouped into key steps of growth, which include the following (Figure 1):^{11,12}

- Formation of a conditioning film: by an initial accumulation of physically adsorbed organic molecules (proteins, polysaccharides, glycoproteins).

- Primary colonization: with the settlement and growth of pioneer bacteria creating a biofilm matrix. First, isolated planktonic bacteria become fixed into heaps on a surface. This adhesion is reversible, as only weak and noncovalent bonds, such as Van der Waals, electrostatic, and acid–base forces, form. Then bacteria irreversibly anchor on the surface *via* a cellular appendix and exopolymers. When the biofilm is mature, it is passed through by liquid currents such as nutrients and can develop at macroscopic scales up to several meters under optimum conditions.

- Secondary colonization: the existence of this microbial film provides sufficient food to allow the fixing of a biofilm of multicellular species (e.g., spores of macroalgae), generally called microfouling (slime).

- Tertiary colonization: which includes the increased capture of particles and organisms, such as larvae of marine macro-organisms. Macrofoulants include macroalgae, sponges, cnidarians, polychaetes, mollusks, barnacles, bryozoans, and tunicates.

However, in practice this sequence of events holds true only for a number of organisms. The sequence of biofouling may not be predictable due to the exploitation of substrate niches by higher fouling organisms.¹³ Biofilm formation is often a precursor to subsequent fouling by macrofoulants. However, the presence of a biofilm is not always necessary, and marine species may settle at the same time. Species such as zoospores of the alga *Ulva linza* and cyprids of the barnacle *Amphibalanus amphitrite* (*A. amphitrite*), previously named *Balanus amphitrite*,¹⁴ can settle on pristine surfaces.

2.1.2. Main Fouling Organisms. Among more than 4,000 fouling organisms identified worldwide,¹⁰ bacteria, diatoms, and algae spores are the main micro-organisms that settle on ship hulls (Figure 2A)^{15–17} while barnacles, tubeworms, bryozoans, mussels, and algae are the most common macro-organisms (Figure 2B).

Barnacles are the most familiar of the arthropods found on ship bottoms, and all successful AF paints must control barnacle fouling. In their adult form, they are encased in hard calcareous shells and are permanently attached to surfaces which are completely submerged or periodically wetted.¹⁸ Barnacles start life as nauplius larvae that feed on plankton and undergo a series of moults. The final larval stage is the cypris larvae or “cyprid”, which is approximately 500 μm in length and does not feed but swims around freely in the water prior to settlement. In order to complete the transition to adult life, these cyprids must attach themselves to a hard substrate. During this exploration phase, the cyprid “walks” over the surface using a pair of attachment organs or “antennules” that secrete a temporary adhesive. Cyprids exploring a surface also

have to be capable of detaching, leaving behind blebs of temporary adhesive “footprints”. The temporary bioadhesive does not disperse in water, is resistant to biodegradation, and also operates as a signaling molecule to induce the settlement of additional cyprids. The firmly attached juvenile subsequently metamorphoses into the calcified adult barnacle.¹⁹ Adult barnacle cement is relatively little-studied and appears to be a complex of hydrophobic proteins cross-linked through disulfide bonds.²⁰ The green alga *Ulva* (formerly *Enteromorpha*) is the most common macroalga contributing to “soft” fouling of man-made surfaces throughout the world and has been extensively used as a model system for experimental studies of biofouling and adhesion.²¹ *Ulva* colonizes new surfaces through the production of vast quantities of microscopic motile zoospores (5–8 μm in length). Once a suitable surface is detected, swimming spores settle and adhere *via* the secretion of a hydrophilic glycoprotein bioadhesive. Spore germination occurs within a few hours, cell division and growth giving rise to sporelings—young plants that are also firmly attached to the substratum by the secretion of bioadhesives.²¹ Diatoms are brown pigmented unicellular algae enclosed in a silica wall. Diatom biofilms are of interest because, as well as being highly resistant to biocidal AF paints, they are especially difficult to remove from nontoxic FRCs.¹⁹ Because most diatoms lack flagella, they cannot actively approach a surface, but they are rather passively carried to surfaces by the action of currents and localized water movement or by settling under gravity.²² As with bacteria, diatoms adhere by secreting large amounts of mucilaginous extracellular polymeric substances which are predominantly composed of polysaccharides. These substances also provide the mechanism for the diatoms “gliding” motility.²³ Then, attached diatoms cells divide, rapidly giving rise to colonies that eventually coalesce to form a compact biofilm, which may reach 500 μm in thickness.²³ Diatom fouling is dominated by a restricted number of genera, and the diatoms *Navicula* and *Amphora* are the most common on biocidal AF and FRCs.^{24–26}

2.1.3. Effects of the Environment on Fouling Colonization. Several factors influence the settlement of marine fouling on surfaces, including salinity, pH, temperature, nutrient levels, flow rates, and the intensity of solar radiation. These factors vary seasonally, spatially, and with depth.^{10,27} The temperature of the surface waters of the oceans varies with the latitude, from about –2 °C at the poles to 28 °C at the Equator, although temperatures up to 35 °C can be reached locally. The salt content of the waters of the open sea, away from inshore influences such as melting ice, freshwater rivers, and areas of high evaporation, is remarkably constant and is rarely outside the range of 3.3–3.8 wt %. Seawater is normally alkaline, and the pH of the surface layers of the ocean, where the water is in equilibrium with atmospheric carbon dioxide, lies between 8.0 and 8.3, and in the open ocean it is, again, a very constant property. In polar areas (temperature lower than 5 °C), the fouling grows in small quantities only during a short period in summer. Colonization and succession of biofouling communities are highly affected by seasonality in temperate regions, with less fouling development in winter due to the reduction in seawater temperature, the intensity of solar radiation, and the numbers of spores and larvae.²⁷ From spring to late summer, nutrient levels and seawater temperature increase, leading to a higher fouling pressure. Few variations of the water temperature and the light intensity are observed in marine tropical and subtropical oceans, resulting in high pressure of fouling

throughout the year.²⁸ Generally, the same major groups of organisms are responsible for fouling worldwide, but the individual dominant species involved tend to vary.²⁷

2.1.4. Effects of Substrate on Fouling Colonization.

The settlement of fouling organisms may be influenced by the substrate on which they adhere. The surface energy of the substrate is one of the most relevant physicochemical parameters influencing the settlement and the adhesion strength of fouling. Although hydrophobic fouling organisms are commonly considered to adhere to hydrophobic materials and hydrophilic ones preferentially stick to hydrophilic substrates, it is difficult to find generalities in the literature due to the wide variety of organisms studied, their various physiological states at the time of the experimentation, and the conditions used.²⁹ Bacterial adhesion may decrease or increase with increasing surface energy of substrates, depending on the physical and chemical properties of bacteria, substrates, and water solutions.^{30–34} In field studies, dominant fouling organisms showed three common patterns in response to surface energy. Bryozoans preferentially settled on surfaces with low energy ($10\text{--}30 \text{ mN}\cdot\text{m}^{-1}$),³⁵ barnacles on surfaces with high energy ($30\text{--}35 \text{ mN}\cdot\text{m}^{-1}$),³⁵ and hydroids in equal proportion on surfaces of all energies.³⁶ However, this general behavior may differ depending on the species. For example, several studies have suggested that cypris larvae of *A. amphitrite* prefer to settle on surfaces of high wettability^{35,37,38} whereas cypris larvae of the barnacle *B. improvisus*, in contrast, prefer to settle on surfaces of reduced wettability or surface energy.³⁹ In the case of green alga *Ulva*, spores have been shown to preferably settle on hydrophobic surfaces⁴⁰ but are only weakly attached and more strongly adhere to hydrophilic surfaces.²⁵ For the diatom *Amphora*, cells accumulate and attach more strongly to hydrophobic surfaces.^{25,41,42} However, the formation of a conditioning film may impact on the physicochemical properties of immersed substrates.⁴³ This approach is still widely debated, since some studies have demonstrated that there is little or no correlation between protein adsorption on surfaces and bacterial adhesion.^{44,45}

Roughness and porosity may also play a role in the settlement of fouling organisms on a surface immersed in seawater, as surface irregularities (anfractuosités) are generated and increase the area of surface that can be colonized, and therefore the number of adhesion sites.^{46,47} The valleys of rough surfaces can be penetrated by marine bioadhesives which cure to create a secure mechanical lock (known as the thigmotactic nature of fouling organisms).⁴⁸ Thus, theoretically, the rougher a coating surface becomes, the more likely it is to be fouled. Moreover, anfractuosités are an adequate environment for the development of bacteria and other marine organisms, as they are protected in these confined areas from exterior aggressions, shear, and abrasion, thus making their removal by hydrodynamical treatment difficult. Nevertheless, well-defined and appropriate topographies can reduce biological adhesion, as discussed in paragraph 3.2.1.

2.2. Impacts of Marine Fouling

The negative effects of marine fouling can be economic, environmental, or safety-related. Accumulations of micro- and macro-organisms generate surface roughness and irregularities which increase the frictional resistance of a boat moving through water and consequently increase fuel consumption and emission of greenhouse gases. Schultz⁴⁹ showed that even slime films can lead to significant increases in resistance and powering

as shown in Table 1. Heavy calcareous fouling can result in powering penalties of up to 86% at cruising speed.

Table 1. Predictions of the Change in Total Resistance (ΔR_t) and Required Shaft Power (ΔS_P) for a Mid-size Naval Ship with a Range of Representative Coating and Fouling Conditions (with Associated Average Coating Roughness (R_{t50})) at Cruising Speed (15 knots)⁴⁹

hull condition	R_{t50} (μm)	ΔR_t (%)	ΔS_P (%)
hydraulically smooth surface	0		
typical as-applied AF coating	150	2	2
deteriorated coating or light slime	300	11	11
heavy slime	600	20	21
small calcareous fouling or weed	1,000	34	35
medium calcareous fouling	3,000	52	54
heavy calcareous fouling	10,000	80	86

The International Maritime Organization estimated that, without corrective action and introduction of new technologies, air emissions due to increased bunker fuel consumption by the world's shipping fleet could increase by between 38% and 72% by 2020.⁵⁰ It is estimated that AF coatings provide the shipping industry with annual fuel savings of \$60 billion and reduced emissions of 384 million and 3.6 million tones, respectively, for carbon dioxide and sulfur dioxide per annum.⁵¹

Another effect of marine fouling is the deterioration of coatings such as favored corrosion, especially in the case of settlement of invertebrates such as barnacles. Barnacles use bioadhesives to provide a strong attachment to the hull, and the growth of their basal edges can penetrate and undermine the protective coatings, leading to premature corrosion. Settlement of fouling results in an increase of the frequency of dry-docking operations, either because of the need of additional hull cleaning or even costly additional coating replacement or hull repair.⁵² Settlement of fouling organisms on hull vessels is also a major issue concerning the introduction of invasive, nonindigenous ("alien") species into non-native environments. Indeed, fouled vessels are the most common vectors of marine species which attach themselves to the ship hull and can be displaced in foreign areas and waters, leading to potential hazard to the local marine environment thus "invaded".⁵³ The impacts of this phenomenon can be, on the one hand, ecological and evolutionary, with direct and indirect competition with native species, effect on higher trophic levels, and change of ecosystem processes. On the other hand, it could have economic and societal impacts, including management costs, impact on human health, and costs for eradication and control measures.²⁷

3. ANTIFOULING TECHNOLOGIES

During the late 1970s, the AF research and development efforts were mainly focused on the successful TBT-based self-polishing copolymer systems. However, due to the emergence of environmental issues associated with TBT compounds, tin-free coatings were developed in the early 1980s.¹⁹ The increasing number of publications, shown in Figure 3, shows the intensification of research on new generations of AF technologies. The current AF strategies can be divided into two main categories: (i) chemically active coatings, which act on the marine organisms by inhibiting or limiting their settlement using chemically active compounds, and (ii) nontoxic coatings, which inhibit the settlement of organisms or enhance the

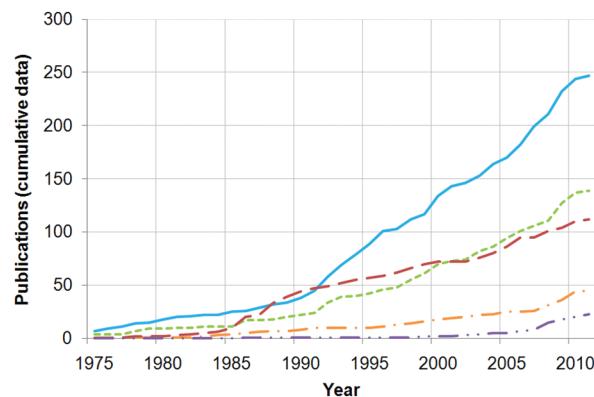


Figure 3. Total publications, papers, and patents on silicone-based coatings (—), fluoro-based coatings (---), self-polishing coatings (— · —), enzyme-based coatings (— · · —), and engineered microtopographical coatings (— · · · —) from 1975 to 2011, based on a SciFinder search of the terms “marine coating or paint”, “silicone or PDMS”, “fluoro or fluoropolymer”, “self-polishing”, and “enzyme” or “topography”, respectively.

release of settled organisms without involving chemical reactions. In the transition period between tin-based coatings and nontoxic AF coatings, the tin-free chemically active self-polishing coatings were claimed as the most efficient coatings in service. Nontoxic FRCs were first patented in 1961 with the use of cross-linked silicone resins as marine coatings, and intensive work has been carried out since the early 1990s related to the development of both silicone- and fluoro-based coatings.⁵⁴ The number of publications which deal with FRC technology has continuously increased and is currently higher than publications concerning the most efficient chemically active paints (i.e., tin-free self-polishing paints). A growing interest in enzyme-based coatings and engineered topographical surfaces as “promising” coatings has appeared in marine applications since the early 2000s, with a number of scientific papers which doubles over the period 2000–2010 for the enzyme-based technology.

3.1. Chemically Active Antifouling Coatings

3.1.1. Biocide-Based Coatings. Chemically active AF technologies are based on the release of tin-free active compounds called biocides and can be subdivided into three main categories: contact leaching coatings, soluble/controlled depletion polymer (CDP) coatings, and self-polishing copolymer (SPC) coatings (Figure 4). All of these technologies take aim at the same objective, the controlled release of bioactive molecules embedded in a polymer matrix called binder, but act with various mechanisms, many of which remain only partially understood.⁵⁵

3.1.1.1. Contact Leaching Coatings (Insoluble Matrix). This type of AF paint uses high molecular weight binders that

are insoluble in seawater, such as acrylics, vinyls, epoxy, or chlorinated rubber polymers.¹⁰ Small amounts of rosin can also be incorporated. In view of their good mechanical strength characteristics, due to which these coatings are also known as hard AF paints, high amounts of toxicants can be incorporated. These active molecules or particles can be in direct contact with each other and, consequently, can be released gradually. Since the binder is not soluble in seawater, as the toxicant agents it contains are released, the seawater spreads through the pores that are left empty by the latter and goes on to dissolve the next toxicant particles. However, as the exposed toxicant particles are deeper in the paint film, the toxicant release rate gradually decreases with time, and the protection becomes increasingly inefficient (Figure 4a). For its part, the honeycomb structure left in the coating contributes to make the surface rougher and more able to retain pollutants from the seawater, a fact that also contributes to prevent toxicants from releasing. For these reasons, the AF efficiency duration of the coatings obtained with these paints is between 12 and 24 months, depending on the severity of the exposure conditions, which limits their use for navy and merchant vessels.⁵⁶

3.1.1.2. Soluble Matrix and Controlled Depletion Polymer Coatings. Also known as ablative/erodible paints, soluble matrix paints contain biocides which are mixed with a large proportion of physically drying, nontoxic, seawater-soluble binder based on high amounts of rosin and its derivatives. In contact with seawater, the biocides and the soluble binder are simultaneously dissolved and released (Figure 4b). Traditional soluble matrix paints do not maintain an AF protection for more than 12–15 months, as the erosion and the release rates are too high during the early immersion period and rapidly decrease thereafter.⁵⁶ Thus, controlled depletion polymer (CDP) coatings were developed. Their binder is reinforced by synthetic organic resins which are more resistant than rosin derivatives and control the hydration and dissolution of the soluble binder. However, their working mechanisms are assumed to be similar to those of conventional rosin-based paints. In contact with seawater, the biocides dissolve together with the soluble binder, and the dissolution process-controlling ingredients are “washed” from the surface.⁵⁶ The key difference between CDP paints and SPC paints is that the ablative mechanism is hydration and dissolution, not hydrolysis. The CDP technology enables effectiveness for periods up to 36 months.

3.1.1.3. Self-Polishing Copolymer Coatings. Self-polishing copolymer (SPC) coatings are based on acrylic or methacrylic copolymers which are easily hydrolyzable in seawater. These copolymers blended with biocides confer a smooth surface of the coating and an ability of controlling/regulating biocides leaching rate through controlling the binder erosion rate.⁹ Fouling organisms, which attach on the surface of a paint film,

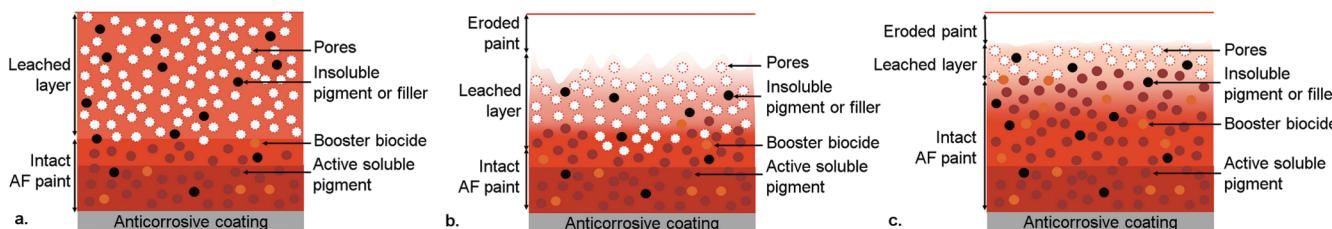
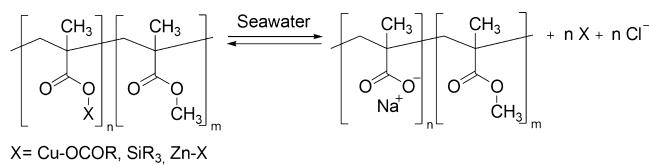


Figure 4. Schematic illustration of the behavior of a biocide-based antifouling system exposed to seawater. (a) Contact leaching coatings; (b) Soluble matrix or Controlled Depletion Polymer coatings; (c) Self-Polishing Copolymer coatings.

are eliminated together with the binder or matrix, which is decomposed by the hydrolysis of the side groups of copolymer chains. The (meth)acrylic copolymers were designed to mimic the well-known organotin-based (meth)acrylic copolymers used in TBT-based AF paints. Tin-free binders use copper, silicon, or zinc-based ester moieties in place of TBT-ester groups. Bressy et al.⁵⁵ recently classified the commercial and experimental binders used in tin-free SPC paints. Such paints undergo the following mechanism when immersed in seawater (Figure 4c): (i) Water diffuses into the coating, leading to the dissolution of the soluble pigment or biocidal particles. As the copolymer matrix is hydrophobic, the water is prevented from penetrating the film. Thus, the seawater barely manages to fill the pores created by the soluble pigment particles. (ii) As the (meth)acrylic ester group is hydrolytically unstable under slightly alkaline conditions, such as those found in seawater, slow and controlled hydrolysis of the coating takes place, according to a reaction confined to a few micrometers from the surface (leached layer), which is represented in Scheme 1.⁵⁶

Scheme 1. General Chemical Structure and Main Reaction with Seawater of Hydrolyzable Poly(meth)acrylic Copolymers



(iii) In time, seawater dissolves more pigment or biocidal particles, causing the growth of the leached area and making the copolymer film brittle and easily erodible by seawater, leaving a new fresh area of the coating uncovered for subsequent release of active molecules (self-polishing effect).⁵⁶ The movement of the pigment front resulting from the pigment dissolution and the ion diffusion through the leached layer becomes equal to the rate of erosion of the binder (related to the polishing rate), so a steady value of the leached layer thickness is reached. This thickness has a remarkably stable and low (10–20 μm) value over the lifetime of the coating.¹⁰ The release rate of biocides in SPCs is controlled by the degree of polymerization (molecular weight) and the hydrophilic character of the copolymer binder, which depends on the proportion of hydrolyzable groups

within the copolymer chains.⁹ SPC paints are typically formulated to have a polishing rate close to 5–20 μm a year, which has allowed dry docking intervals to be extended up to periods of 5 years.⁵⁶

3.1.1.4. Hybrid Ablative-Self-Polishing Systems. Hybrid AF systems combine the hydrolyzable SPC technology together with the rosin-based CDP technology.⁵⁷ The biocide release relies on both hydrolysis and hydration mechanisms. These hybrid AF paints exhibit the CDP features of surface tolerance and attractive volume solids, together with the SPC benefits of polishing rate and biocide release control, and reduced leached layer thickness. Their AF effectiveness generally lasts between 3 and 5 years.

3.1.1.5. Biocides. Following the ban of TBT-based products in AF paints, alternatives containing high amounts of copper (Cu)-based compounds were developed. As it is about ten times less toxic than TBT, cobiocides, also called boosters, were used to enhance the AF performance of copper-based coatings.⁵⁸ The potential of biocidal compounds to cause adverse effects has received major attention, and biocide-containing AF paints are currently regulated and require approval. As a consequence of the growing investigations on its toxicity, the release rate of Cu-based soluble species from AF paints has been regulated in several areas, for example, Sweden⁸ and the U.S. states Washington and California.^{59,60} Since 2000, in the European Union, the Biocidal Products Directive (98/8/EC) regulates the production, marketing, and use of non-agricultural products intended for biocidal purposes, such as biocides in AF coatings (annex I/IA).⁷ Table 2 gives a list of the main biocides currently used in AF paints as well as new candidate biocides not yet mentioned in the Biocidal Products Directive. All these compounds vary in terms of their mode of action, environmental persistence, and toxicological properties. Several reviews have been published presenting an overview of the biocides used in AF paints and their specific fate and effects in the environment.^{9,61–65}

The key property of a good AF biocide with respect to the environment is that it is effective in preventing fouling of the painted surface without persisting at concentrations greater than those that can cause detrimental environmental effects.⁶³ Environmentally benign alternatives to control surface colonization have been investigated. They exploit natural marine product antifoulants utilized by marine organisms to prevent themselves from colonization by other marine

Table 2. Main and New Candidate (*) Biocides Used in Antifouling Paints (See Chart 1)

biocide	alternative name	CAS number
copper		7440-50-8
dicopper oxide (cuprous oxide)		1317-39-1
copper thiocyanate 1		1111-67-7
bis(1-hydroxy-1H-pyridine-2-thionate-O,S) copper 2		14915-37-8
zinc complex of 2-mercaptopyridine-1-oxide 3		13463-41-7
N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfamide 4		1085-98-9
N-dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide 5		731-27-1
4,5-dichloro-2-n-octyl-4-isothiazolin-3-one 6	Sea-Nine 211, Kathon 287T, Kathon 930, DCOIT	64359-81-5
zinc ethylene bisdithiocarbamate 7	Zineb	12122-67-7
N'- <i>tert</i> -butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine 8	Irgarol 1051, Cybutryne	28159-98-0
triphenylboron pyridine complex 9 (*)	TPBP	971-66-4
2-(<i>p</i> -chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole 10 (*)	Tralopyril, Econea	122454-29-9
N-[4-hydroxy-3-methoxyphenyl)methyl]-8-methylnon-6-enamide 11 (*)	Capsaicin	404-86-4
4-[1-(2,3-dimethylphenyl)ethyl]-3H-imidazole 12 (*)	Medetomidine, Selektope	86347-14-0

Chart 1. Main Biocides Used in Antifouling Paints

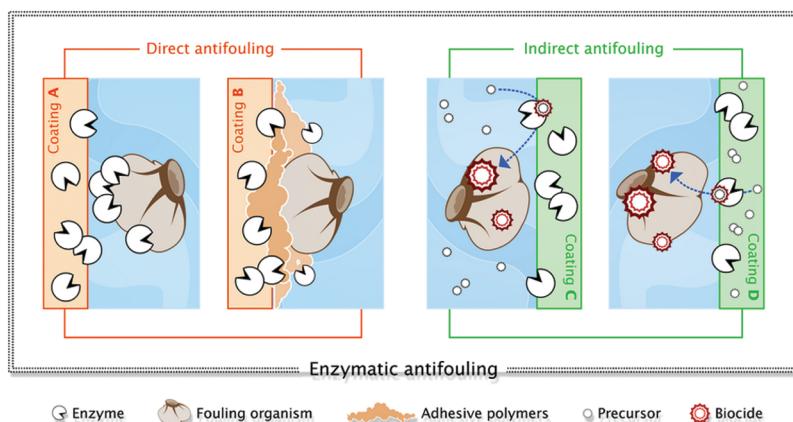
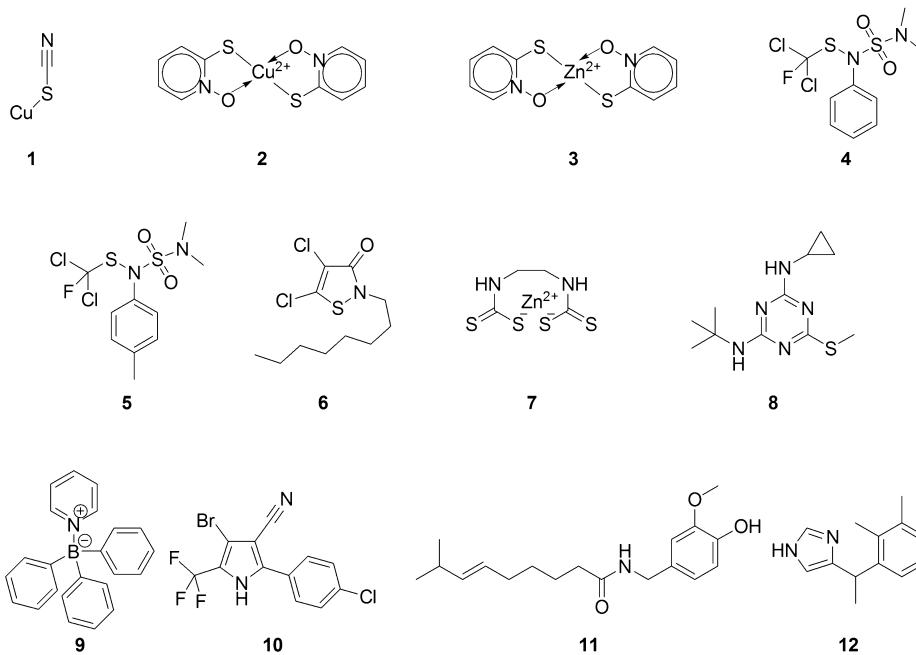


Figure 5. Classification and proposed mechanism of enzymatic antifouling. Coating A is based on biocidal direct antifouling. Coating B is based on adhesive degrading direct antifouling. Coating C is based on indirect antifouling with substrate in the environment. Coating D is based on indirect antifouling with the substrates provided from the paint. Reprinted with permission from ref 73. Copyright 2009 Woodhead Publishing.

organisms (e.g., sponges, corals, and macroalgae).^{66–69} To date, purification of active products has yielded *ca.* 200 molecules with some degree of AF activity against a wide range of marine fouling organisms, assayed mainly through laboratory tests.⁶⁹ The challenge of finding a natural product which fulfills the required criteria of low toxicity, broad-spectrum activity, and ease of production has yet to be realized and is the main reason why they have not been so far successfully commercialized. Moreover, Maréchal and Hellio²⁸ pointed out that the regulatory authorities now require testing of new active substances before marketing authorization. The total costs have to be taken into account, including preparing agreed protocols and placing studies, but also monitoring studies, analysis of the results, risk assessments based on exposure scenarios, dossier preparation, registration costs, task force participation, legal fees, etc., as well as management activities of the directive and associated registration. For the development of new antifoulants, the estimated costs are as followed: toxicity studies on active substances, 1–3 M€; environmental studies

and ecotoxicity, 0.6–4 M€; formulation studies, >1 M€; risk assessments/exposure scenarios expertise needed, >1 M€; dossier preparation, 0.1–0.25 M€; registration fees, 0.1–0.2 M€; task forces, 0.05–0.2 M€.²⁸

3.1.2. Enzyme-Based Coatings. The idea of using enzymes for AF coatings emerged during the 1980s,⁷⁰ and the concept has received increased interest in recent years.^{71,72} Enzymes are catalytically active proteins and are omnipresent in nature. They can degrade the fouling organism or its bioadhesive, or produce other biocidal compounds. Olsen et al.⁷³ divided the enzyme approaches into direct and indirect enzymatic AF, depending on the nature of the enzymes and substrates. Direct enzymatic AF covers the application of “biocidal” or adhesive-degrading enzymes, whereas indirect enzymatic AF is based on enzymatic generation of biocides from substrates present in seawater or coating-ingredients. The overall classification of mechanisms applied in enzymatic AF coatings is presented in Figure 5. Olsen et al.⁷¹ proposed four requirements for enzyme-based AF systems: (1) Enzymes must

retain activity when mixed with coating components. (2) Enzymes must not deteriorate coating performance. (3) Enzymes must have a broad-spectrum AF effect. (4) Enzyme activity must have long-term stability in the dry coating and after submersion of a coated surface in the sea.

The adhesive-degrading enzyme direct AF is one of the most widely suggested approaches and uses proteases and glycosylases to break down the bioadhesive based on protein and polysaccharide components.⁷² A variety of commercially available enzymes has been explored as nontoxic antifoulants, such as Alcalase, a commercial preparation of the serine endopeptidase Subtilisin A.^{71,72,74,75} This enzyme has the advantages of being readily available, nontoxic, and biodegradable. Several proteases and carbohydrazes have been reported to inhibit the settlement of *Bugula neritina* larvae, *A. amphitrite* larvae, *Ulva linza* spores, and the diatom *Navicula perminuta* (*N. perminuta*).^{74,76,77} Proteases, mainly Subtilisin, have been shown to inhibit biofilm formation by cultures of marine bacteria *Pseudoalteromonas* sp. D41^{75,78} or *Pseudomonas fluorescens*⁷⁹ and by cocultures of four marine bacteria.⁸⁰ In several cases, concepts as well as short-term AF activity in coatings have been proven, but long-term efficiency toward all fouling organisms remains to be reported. Moreover, according to the definition of biocides in the Biocidal Products Directive, an enzyme known to act on the bioadhesive of fouling organisms is determined to be within the scope of the directive, and therefore, enzymes will have to undergo registration similar to that for conventional biocides.

3.2. Nontoxic Coatings

3.2.1. Engineered Microtopographical Surfaces. One of the nontoxic AF strategies is to disrupt physically the adhesion of marine organisms by the use of microtopographical surfaces, as it is employed by natural organisms in their defense against bioadhesion.^{81,82} Microtopography has been shown to deter biofouling on marine mammal,⁸³ shark skin,^{84–86} or mollusk shells^{81,87} and affect attachment of barnacles,^{85,88} algae,^{84,89} and bacteria.⁹⁰ While these studies demonstrated the AF potential of microtopographical surfaces in the marine environment, the underlying mechanism responsible for reduced fouling (i.e., settlement and attachment) still remains unclear. The change of surface wettability that results from topography may be a contributing factor to these responses.⁹¹ It has also been suggested that microtopographies might influence surface near-fluid dynamics and thus microhydrodynamically prevent settlement.⁴⁷ Nevertheless, the most developed concept assumes that adhesion strength is related to the number of attachment points of the marine organism on the surface (Figure 6).^{92,93} When fouling organisms are at the attachment phase, they vary considerably in shape and size. Bacteria ($\approx 1 \mu\text{m}$), diatoms (3–15 μm), and algal spores (5–10 μm) are considered to be the major microfouling organisms, and tubeworms, bryozoans, ascidians, and barnacle larvae (120–500 μm) are the major macrofouling organisms found on immersed substrates. Both types of foulants are influenced by a vastly different scale of topography. A common mechanism for attachment preferences is the number of attachment points a surface provides. Fouling organisms that are larger than the primary length scale of the surface texture generally exhibit reduced adhesion strength, as there are fewer attachment points. Conversely, when settling on surfaces with topographic features of larger length dimensions, i.e. larger than the cell or organism, more attachment points are presented, thereby

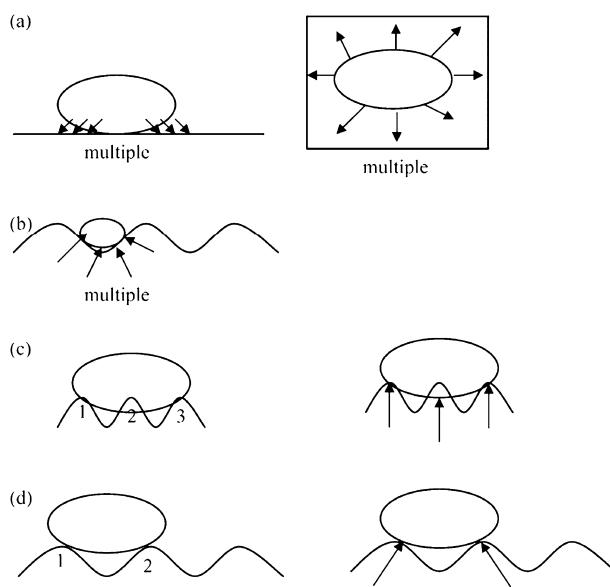


Figure 6. Illustration of the attachment points theory for diatoms: (a) stronger adhesion strength (multiple attachment points) for all diatoms on a smooth surface, (b) for *F. carpentariae* on 2 mm ripples (lower adhesion strength; least attachment points), (c) for *N. jeffreyi* on 2 mm ripples, and (d) for *Amphora* sp. on 4 mm ripples. Reprinted with permission from ref 92. Copyright 2006 Taylor & Francis Group.

facilitating stronger adhesion. This attachment point theory has been recorded for spores of the green algae *Ulva linza*,^{86,89,94} for four species of diatoms,⁹² for the tubeworm *Hydroides elegans* and the bryozoan *Buluga neritina*,⁹³ and for *A. amphitrite* cyprids.⁹⁵

The most common methods used to produce microtopographical surfaces are laser ablation,^{92,93,96} photolithography,^{86,97} or molds and casting,^{81,98} and they have generally been applied to substrates of poly(dimethylsiloxane) (PDMS), poly(vinylchloride) (PVC), polycarbonate, or polyimide.⁹⁹ Figure 7 gives some examples of engineered topographies on a PDMS surface.

Engineered microtopographies were shown to reduce *Ulva* spores settlement by up to 58% (2 μm diameter pillars and 10 μm pyramids) and by 77% for microtopographies replicating shark skin.^{84,86} Barnacle settlements were reduced by almost 100% on a microtextured PVC surface even though the smooth PVC received the strongest settlement out of all materials tested biocides-based AF coatings and FRCs together with some in its smooth state.⁸⁸ Petronis et al.¹⁰⁰ showed that PDMS surfaces microtextured with large riblets inhibit the settlement of barnacle *B. improvisus* up to 67%. Brennan's research team concluded that the settlement of *A. amphitrite* cyprids on a textured PDMS surface was directly related to the aspect ratio of the surface features.⁸⁵ They demonstrated a negative correlation between the settlement behavior of the spores of *Ulva* and a newly described dimensionless Engineered Roughness Index ratio based on three variables which reflect the size, geometry, and spatial arrangement of the topographical features.⁸⁴ Genzer and Efimenko¹⁰¹ suggested that a topographical pattern having a single length scale will not likely perform as a generic AF surface, since biofouling includes marine organisms with sizes of several orders of magnitude (cells, spores, larvae). Thus, hierarchically wrinkled coatings having nested wrinkles of different length scales ranging from tens of nanometers to a fraction of a millimeter were

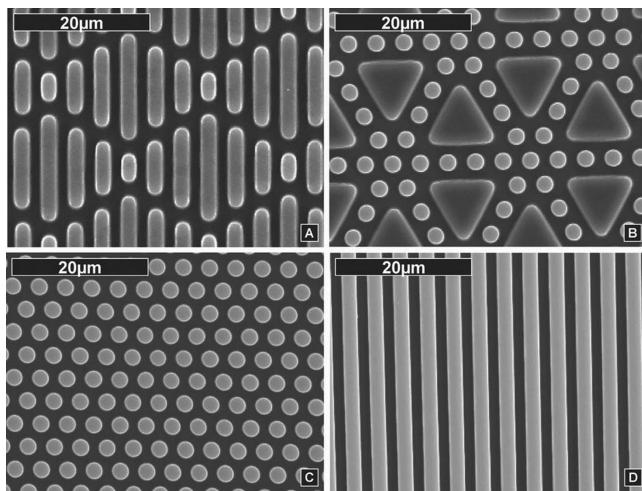


Figure 7. SEM images of engineered topographies on a PDMS surface. (A) 2 μm ribs of lengths 4, 8, 12, and 16 μm combined to create the Sharklet AFTM; (B) 10 μm equilateral triangles combined with 2 μm diameter circular pillars; (C) hexagonally packed 2 μm diameter circular pillars; (D) 2 μm wide ridges separated by 2 μm wide channels. Reprinted with permission from ref 84. Copyright 2007 Taylor & Francis Group.

developed.¹⁰² These coatings remained relatively free of biofouling including barnacles even after 18 months of exposure to seawater compared with the equivalent flat surfaces.

3.2.2. Fouling Release Coatings. Fouling release coatings are biocide-free coatings, and their AF performances rely on a dual mode of action, i.e. nonstick properties and a FR behavior. The general idea of FRCs is to minimize the adhesion between fouling organisms and the surface, so that the fouling can be removed by hydrodynamic stress during navigation or by a simple mechanical cleaning.^{103,104} The self-cleaning properties of FRCs are illustrated in Figure 8, where an initially fouled FRC-coated surface is able to self-clean at different velocities. Moreover, the smoothness of FRCs enables them to reduce the drag of the vessel and therefore reduce fuel consumption and greenhouse gas emissions. In the patented and scientific literature, FRCs include both silicone- and fluoropolymer-based binders, as they are the two major polymeric materials reported to exhibit FR properties.

Currently, commercially available FRCs are generally developed as a duplex system composed of a FR top-coat and a tie-coat applied on an anticorrosive epoxy primer. The top-coat is based on cross-linked PDMS elastomers and usually contains additive oils to enhance their slippery nature. The tie-

coat is required to promote the adhesion between the nonstick FR top-coat and the epoxy primer (Figure 9).

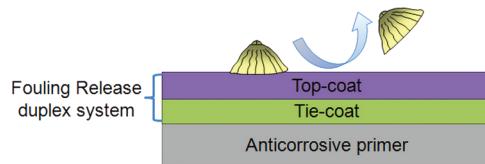


Figure 9. Schematic illustration of FR systems.

The specific FR properties have traditionally been related to the surface hydrophobicity and low energy but are also influenced by other parameters, including surface roughness, elastic modulus, and thickness of the film coating. This will be discussed in more detail in paragraph 4. The reported lifetime in service of FRCs is typically 5–10 years.

3.3. Comparative Performances

The biocide-based AF coatings and FRCs are the two technologies currently available on the global marine coatings market. The major difficulties preventing the commercialization of microtopographical surfaces are the price and the impractical use for large vessels. To our knowledge, only one enzyme additive for water- or solvent-based paints, called CoatZyme, is currently commercialized by Biolocus for the yachting market. The total sales of FRCs rose significantly following the adoption of the International Maritime Organization convention in 2003, and they are currently estimated to be 10% by volume for commercial shipping but remain at less than 1% in the yacht sector.¹⁰⁵ Yebra and Catalá¹⁰⁶ estimated that a hypothetical complete conversion to FRCs would save more than 70 million tones of copper-based biocides, 6 million tones of booster biocides, and 20 million liters of solvent per year in the word. One of the advantages of a FR system is their high volume solid content (*ca.* 70%) compared to SPC coatings (40–50%) and CDP coatings (50–60%), reducing solvent emissions in the shipyard.^{106,107} Furthermore, only one top-layer is required compared to two or three layers for biocidal AF coatings. This leads to less time in docks, lower consumption of paints, and lower application costs. FRCs are reported as inherently smoother surfaces than the previous technologies, resulting in a lower drag resistance, at least initially, since fuel savings due to smoothness can be negated if the FR coating becomes fouled.^{108,109} Corbett et al.¹¹⁰ compared the fuel consumption of two vessels (a tanker and a bulk cargo vessel) in the cases where their hulls were coated with tin-free SPC coatings and with a FRC. Results indicated that the application of the FRC reduced speed-adjusted fuel oil

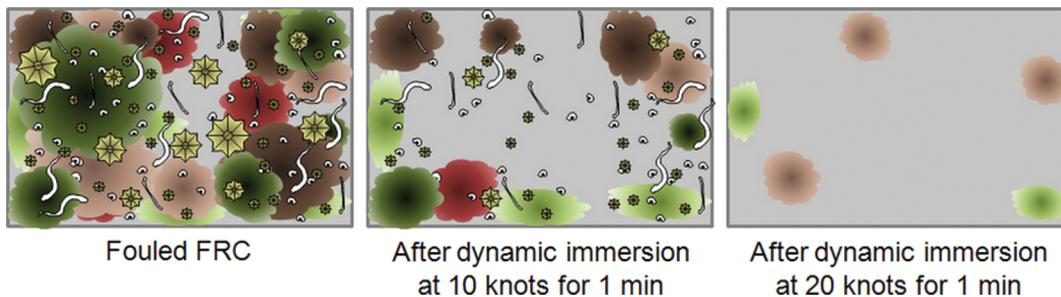


Figure 8. Schematic illustration of the self-cleaning ability of FRCs.

Table 3. Comparative Performances and Prices of the Main Commercially Available Antifouling and Fouling Release Technologies

antifouling technology	mode of action	advantages	disadvantages	assumed paint lifetime (year)	relative paint cost (%)	estimated overall application cost (*)
contact leaching coatings	- high biocides content incorporated in high molecular weight insoluble matrices, low amount of rosin - rely on dissolution of water-soluble biocides	- good mechanical strength	- biocides release decreased with immersion time as did AF performance - biocides released into the environment - subjected to biocidal legislation	1–2	1.5	50 \$/m ²
soluble matrix and controlled depletion polymer coatings	- biocides mixed with a soluble matrix based on high amounts of rosin. - rely on physical dissolution of the paint film to release biocides	- relatively low cost/m ² compared with SPC coatings	- biocides release difficult to control, not constant. - low activity during idle periods - problems recoating at next dry-docking due to skeletal film left at surface - biocides released into the environment - subjected to biocidal legislation	≤3	1.5	15.2 \$/m ² /year
tin-free SPC coatings	- hydrolyzable (meth)acrylate polymers combined with biocides - rely on chemical hydrolysis of matrix	- constant biocide release rates over time (at fixed speed) AF activity during idle periods - polishing leads to surface smoothing, reducing fuel consumption - long lifetime (5 years)	- not as efficient as TBT-SPC coatings - biocides released into the environment - subjected to biocidal legislation	5–10	2–3	75 \$/m ²
fouling release coatings	- low surface energy and minimally adhesive smooth surfaces	- reduced adhesion strength of fouling organisms - no released biocides, so not affected by biocidal legislation - smooth surface leads to drag reduction and fuel saving - only 1 top-coat required compared to 2–3 coats for biocide-based AF coatings - low VOC	- higher initial cost of paint and application - self-cleaning not efficient at speed lower than 8 knots - susceptible to mechanical damage - diatoms slimes difficult to remove even at high speed (30 knots) - long life efficiency (5–10 years)	4–6	116 \$/m ²	11.6 \$/m ² /year

*From Eliasson.¹¹¹

consumption by 10% for the tanker and by 22% for the bulk cargo vessel. They estimated that if similar fuel efficiencies were realized by all tanker and bulk cargo vessels in the international fleet, annual fuel oil consumption could be reduced by roughly 16 million metric tons per year, fuel expenditures could be reduced by \$4.4 to \$8.8 billion per year, and nearly 49 million metric tons of carbon dioxide emission could be avoided annually.

Table 3 summarizes the advantages and disadvantages of biocide-based AF coatings and FRCs together with some current costs. Information about prices of AF systems is not easily accessible, as paint manufacturers are unwilling to openly share such information. All of the major paint types are more expensive than the previously available TBT-SPC AF paints, and on a volume basis, FRCs are more expensive than tin-free SPC technologies, which are more expensive in turn than hybrid, CDP, and contact leaching coatings.¹¹¹ It is generally estimated that FRCs are three times more expensive than tin-free SPC coatings. The typical price of the FRC top-coat is in the range of \$100–150/L^{112,113} compared with that of SPC paints, at \$30–40/L.^{113,114} However, the overall cost associated with a FR or biocidal coating depends not only on the cost of the liquid paint but also on other pertinent parameters, including the off-hire for the vessel, dry-dock hire, hull cleaning, and surface preparation,¹¹¹ as well as the overcosts associated with increased roughness and fouling growth during service life. A method of determining the costs associated with a fouling release or biocidal coating composition during the in-service period of a vessel has been patented in 2004.¹⁰⁹ The increase in roughness and fouling growth results in a 10.0% higher fuel consumption for CDP, after a 3-year service life, and 10.0%, 4.8%, and 1.4% for hybrid SPC, SPC coatings, and FRC, respectively, after a 5-year service life. Therefore, the overall costs per square meter, per year, estimated by Eliasson,¹¹¹ show that the FRCs are in fact globally less expensive than SPC AF products. Even if a 10-year lifetime was estimated for the FRC (whereas a lifetime of 5 years is more often specified), this technology is still less expensive than that of biocidal AF coatings, considering the benefits of fuel savings in operation.^{113,115}

4. FOULING RELEASE COATINGS (FRCs)

4.1. Remarkable Properties of Fouling Release Coatings

4.1.1. Fouling Release Ability. **4.1.1.1. Parameters Influencing the Bioadhesion.** The adhesion to and growth of organisms on surfaces are known to be dictated by the energetics of the interface.⁹¹ Both chemical, physical, and mechanical parameters are involved in the mechanism of bioadhesion. Brady and Singer¹¹⁶ mentioned that the prevention of fouling adhesion may rely on four mechanisms: (1) *Chemical bonding*: Dipolar, ionic, or covalent bonds may be discouraged by creating a surface of nonpolar and nonreactive functional groups and creating conformationally mobile surfaces, which prevent functional groups of marine bio-adhesives from reacting with the substrate. (2) *Electrostatic interactions and physical adsorption*: Surface charge and van der Waals forces may be lowered by ensuring the absence of heteroatoms and polar and ionic groups from the surface of the coating to prevent interactions between the surface and bio-organisms or secreted bioadhesives. (3) *Mechanical interlocking*: When material surfaces are rough and porous, bioadhesives may attach even in the absence of chemical compatibility by

penetrating into surface cavities and locking into them. This mechanical process may occur even if the bioadhesive does not wet the surface. It can be prevented by creating surfaces as smooth and as impenetrable as possible. (4) *Diffusion*: Marine bioadhesives may induce movement in surface molecules, creating temporary microvoids that may then be infiltrated by the bioadhesive. Diffusion may be prevented by assembling on the surface oriented, closely packed functional groups, and cross-linking them to prevent rearrangement and infiltration of the bioadhesive.¹¹⁷

The wetting theory partly influences the bioadhesion mechanism. A thermodynamic model was established to describe the adhesion of a micro-organism to a surface in which the free energy of adhesion (ΔG^{adh}) is related to the interfacial energies between the substrate, the marine organism, and the surrounding liquid (eq 1).^{15,33}

$$\Delta G^{\text{adh}} = \gamma_{\text{BS}} - \gamma_{\text{BL}} - \gamma_{\text{SL}} \quad (1)$$

where γ_{BS} is the interfacial energy between the biofouling organism and the substrate, γ_{BL} is the interfacial energy between the biofouling organism and the surrounding liquid, and γ_{SL} is the interfacial energy between the substrate and the liquid. The adhesion of bacteria³³ and of spores of green alga *Ulva linza* was explained by this model.⁴⁰ Most difficulties come from the experimental determination of the interfacial energy values. Models described in the literature deal with the estimation of interfacial energies and surface energies by wetting investigations using contact angle (CA) measurements. Young's theory, well-known for 200 years, describes the equilibrium condition of a liquid droplet, surrounded by its vapor, placed in contact with a smooth solid surface (Figure 10).¹¹⁸

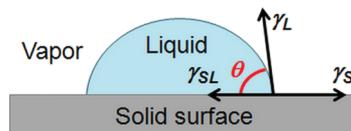


Figure 10. Young's theory.

The shape of the droplet is defined by the contact angle θ (deg), which depends on the surface tension of the liquid γ_L ($\text{mN}\cdot\text{m}^{-1}$), the surface energy of the solid γ_s ($\text{mJ}\cdot\text{m}^{-2}$ or $\text{mN}\cdot\text{m}^{-1}$), and the solid/liquid interfacial energy γ_{SL} ($\text{mJ}\cdot\text{m}^{-2}$ or $\text{mN}\cdot\text{m}^{-1}$) as follows (eq 2):

$$\gamma_L \cos \theta = \gamma_s - \gamma_{\text{SL}} \quad (2)$$

When the liquid used is water, the water contact angle θ_w can be related to the hydrophobic/hydrophilic character of a solid surface: $\theta_w < 90^\circ$ corresponds to a hydrophilic surface and $\theta_w > 90^\circ$ to a hydrophobic surface while $\theta_w > 150^\circ$ leads to superhydrophobic surfaces. The general rule states that the lower the water CA the stronger the interaction (Figure 11).

Considering Young's equation to calculate the surface energy γ_s of a solid, γ_{SL} needs to be assessed. Owens-Wendt, Rabel, and Kaelble¹¹⁹ suggested that the surface energy is equal to the sum of a dispersive component (γ_s^D) and a polar component (γ_s^P) (eq 3). The first one (γ_s^D) reflects the dispersion interactions occurring at the interface, whereas the second one (γ_s^P) reflects polar, hydrogen, inductive, and acid–base interactions. These parameters are related to γ_{SL} using eq 4.

$$\gamma_s = \gamma_s^D + \gamma_s^P \quad (3)$$

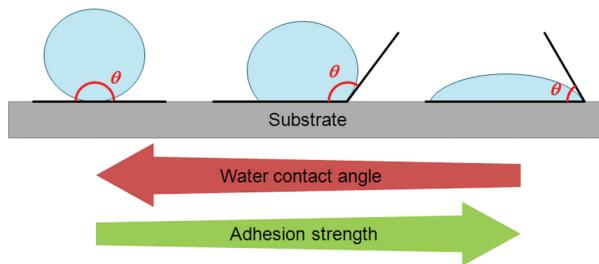


Figure 11. Schematic view showing the influence of the water contact angle on the strength of adhesion.

$$\gamma_{SL} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^D \gamma_l^D} - 2\sqrt{\gamma_s^P \gamma_l^P} \quad (4)$$

where γ_l^D and γ_l^P are the dispersive and polar force contributions to the surface tension γ_l of the liquid used. Combining eqs 2 and 4, γ_s^D and γ_s^P can be calculated from the measurement of the contact angle made by two different liquids on the solid surface as follows (eq 5):

$$\gamma_l(\cos \theta + 1) = 2\sqrt{\gamma_s^D \gamma_l^D} + 2\sqrt{\gamma_s^P \gamma_l^P} \quad (5)$$

Water, glycerol, thiodiglycol, and formamide are the most useful liquids for determining polar–polar and hydrogen bonding interactions, while methylene iodide, bromonaphthalene, and methylnaphthalene are best for the dispersive and π -bonding interactions of aliphatic and ring structures, with the normal alkanes in descending order from hexadecane through pentane best utilized for the purely dispersive interactions.¹²⁰ Later, van Oss, Chaudhury, and Good^{121,122} initiated an acid–base approach for the surface energy calculation assuming that the surface energy is the sum of a Lifshitz–van der Waals apolar component γ_i^{LW} and a Lewis acid–base polar component γ_i^{AB} (eq 6):

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (6)$$

The acid–base polar component γ_i^{AB} can be further subdivided by using specific terms for an electron donor (γ_i^-) and an electron acceptor (γ_i^+) subcomponent (eq 7):

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-} \quad (7)$$

The solid/liquid interfacial energy is then given by eq 8:

$$\gamma_{SL} = \gamma_s + \gamma_l - 2(\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+}) \quad (8)$$

These Lifshitz–van der Waals and acid–base approaches related to the surface energies were also taken into consideration during the bioadhesion of marine benthic diatoms on man-made surfaces.¹⁵ The Lifshitz–van der Waals attractive forces could facilitate the process of adhesion, and the Lewis acid–base forces could be responsible for hydrophobic/hydrophilic interactions. Recently, Liu and Zhao¹²³ demonstrated that the interaction energy between marine bacteria and a substrate has a strong correlation with the ratio of the Lifshitz–van der Waals apolar component to the electron donor component of the surface energy of the substrate (γ_s^{LW}/γ_s^-). However, the adhesion of marine organisms has been historically related to the critical surface tension of the substrate γ_C , which was introduced by Zisman.¹²⁴ This parameter corresponds to the surface tension γ_l of a liquid, which perfectly wets the solid surface, i.e. $\theta = 0^\circ$. γ_C is estimated by measuring the contact angle of a series of liquids placed on the

solid surface and then plotting the cosine of the angle versus the surface tension of the respective liquids and extrapolating to $\theta = 0^\circ$ by means of a best linear fit. The liquids with surface tension γ_l below the γ_C value of the solid are completely spread on the surface. The Zisman approach has attracted controversy, as the γ_C value is largely dependent on the nature of the liquids used. Besides, γ_C is equal to the solid surface energy γ_s only if the solid surface and the liquids used are totally apolar, which is rarely the case. In the literature, an empirical relationship between γ_C and the relative amount of bioadhesion has been established and is commonly known as the Baier curve (Figure 12). This relationship has been confirmed in biomedical

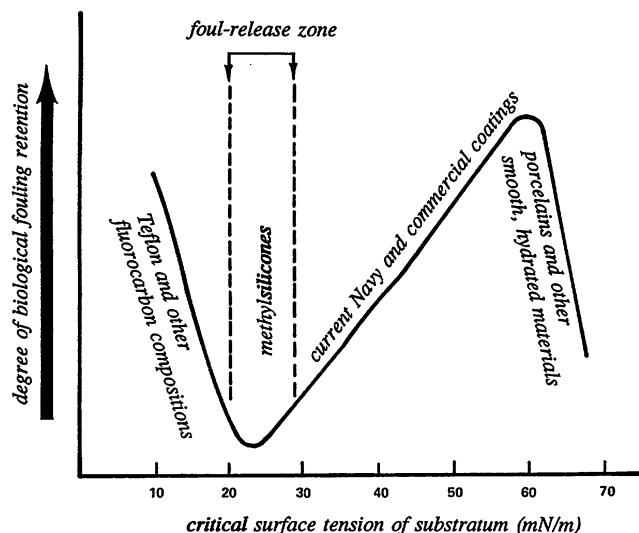


Figure 12. “Baier” curve which represents the empirical relationship between critical substratum surface tension and relative fouling retention. Reprinted with kind permission from ref 120. Copyright 2006 Springer Science & Business Media.

applications¹²⁵ and also in a variety of marine exposure studies.^{30,31,126} The key feature of this curve is that the minimum in relative adhesion at 22–24 mN·m⁻¹ does not occur at the lowest critical surface energy. In fact, the relative adhesion is at a minimum when the interfacial energy γ_{SL} is at a minimum value. Interfacial energy may be diminished by matching the critical surface tension values of the coating surface and the adherend and by reducing the interactions of the bioadhesive with the surface and with water.¹¹⁷ However, Schrader¹²⁷ suggested that the minimum adhesion in water occurs at a surface energy equal to the dispersive component γ_l^D of the surface tension of water, i.e. 22 mN·m⁻¹. In this analysis the available dispersion force from the surface is nearly zero at this point; thus, the dispersion interaction between the bioadhesive and the interface will also be approximately zero and adhesion will consequently be at a minimum.¹¹⁶ In addition, Baier defined the notion of θ surface condition for low bioadhesion, displayed by critical surface tension of 22–24 mN·m⁻¹.¹²⁰ Polymers which fulfill this requirement are polysiloxane or silicone elastomers (e.g., PDMS and poly(-methylphenylsiloxane)) have surface energies of 20 and 26 mN·m⁻¹, respectively.¹²⁸

Furthermore, the prevention of surface rearrangement is another parameter which could limit the infiltration of secreted bioadhesives and consequently the marine organism adhesion. Contact angle hysteresis $\Delta\theta$ is a convenient measure of surface

reorganization when observed over time. Hysteresis is also attributed to surface roughness and chemical heterogeneity.¹²⁹ This parameter is defined as the difference between advancing and receding CAs. The advancing CA θ_{adv} is obtained by placing a liquid drop on a horizontal, flat, nondeformable surface and forcing the liquid to flow; withdrawing the liquid yields a receding angle θ_{rec} (Figure 13). In terms of energetics, CA hysteresis may also be defined as $\gamma_L(\cos \theta_{\text{rec}} - \cos \theta_{\text{adv}})$, where γ_L is the surface tension of the wetting liquid.¹³⁰

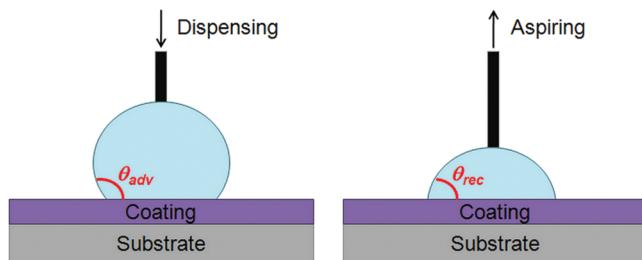


Figure 13. Measurement of dynamic contact angles by the dispensing/aspirating technique.

The advancing water CA is known to be sensitive to the hydrophobic surface component whereas the receding CA is sensitive to the hydrophilic surface component. Although for surfaces with the roughness carefully controlled on the molecular scale it is possible to achieve CA hysteresis as low as 1°, it cannot be eliminated completely, since even atomically smooth surfaces have a certain roughness and heterogeneity.¹³¹ Schmidt et al.¹³⁰ reported that the adhesive properties of a surface were better correlated with water receding CAs and the CA hysteresis than the static or advancing CAs, representing the surface energy. Smoothness is also an important factor influencing the settlement of fouling organisms, since the surface area available for adsorption and attachment of fouling organisms increases with decreasing smoothness (or increasing roughness). The valleys of rough surfaces are penetrated by marine adhesives, and hence, foulants will more readily attach.³ Moreover, the fouling organisms also find shelter from shear and abrasion in the crevices, and thus, roughness also poses a threat to the hydrodynamic removal of the organisms.¹³² Even if the adhesion has been frequently demonstrated to be lesser on smooth and low-energy surfaces,^{30,133–135} contradictory results have been reported.^{25,32,33,40} For instance, marine organisms such as *Ulva* spores⁴⁰ and bryozoans³⁵ prefer settling on low-energy surfaces, and barnacles have been shown to prefer flat surfaces rather than rough surfaces.⁸⁸

Actually, if the adhesion occurs between organisms and low-energy surfaces such as polysiloxane surfaces, only weak dispersive interactions will take place, and consequently, the organisms will be easily removed from the substrate. Therefore, the performance of FRCs seems to preferentially rely on their FR properties rather than their ability to inhibit the settlement of marine organisms.

4.1.1.2. Parameters Influencing the Fouling Release Properties. **4.1.1.2.1. Fracture Theory.** The most useful theory for studying bioadhesion has been the fracture theory, which analyzes the forces required to separate two surfaces after adhesion. Chung and Chaudhury¹³⁶ demonstrated that the mechanisms underlying the release of foulants from soft films can be understood, at least qualitatively, in the light of the Kendall's studies,¹³⁷ where fracture mechanics are used to

assess the release behavior of elastomers. Fracture mechanics is the study of the process of breaking joints. This discipline assumes that no joint is entirely free of defects and that the cracks that exist on a microscopic scale are stress-raisers where the growth of a crack is initiated. The three kinds of crack-opening modes considered in fracture mechanics are shown in Figure 14: peel, in-plane shear, and out-of-plane shear. Failure in peel mode requires less energy than failure in shear mode, and most adhesive joints usually fail in peel mode.¹³⁸

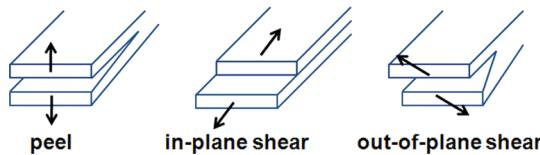


Figure 14. Fracture mechanisms for failure of a joint.

Kendall¹³⁷ showed that the pull-off force, P_c , required to remove a rigid cylindrical stud, of radius a , from an elastomeric

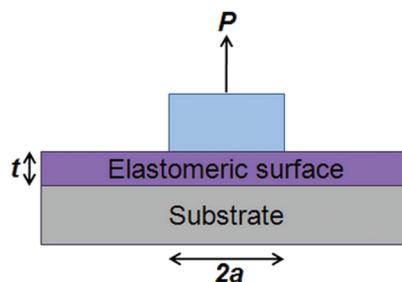


Figure 15. Elastomeric coating held between a rigid substrate and a rigid disk (P = normal force, a = contact radius, t = film thickness).

glue film, of thickness t , attached to a stiff substrate (Figure 15) under conditions that $a/t \gg 1$ is given by (eq 9):

$$P_c = \pi a^2 \left(\frac{2w_a K}{t} \right)^{1/2} \quad (9)$$

where w_a and K are Dupré's work of adhesion between the cylinder and the elastomer, and the bulk modulus, respectively. The bulk modulus is related to the elastic modulus, E , and the Poisson's ratio, ν , as follows (eq 10):

$$K = \frac{E}{3(1 - 2\nu)} \quad (10)$$

This equation of P_c , however, applies to situations where the contact radius a is much larger than the coating thickness. If the film thickness is much greater than the contact radius, i.e. $a/t \ll 1$, then the pull-off force, P_c , is independent of the thickness (eq 11):

$$P_c = \pi a^2 \left(\frac{8Ew_a}{\pi a(1 - \nu^2)} \right)^{1/2} \quad (11)$$

These equations make clear that fracture or removal processes involve not only the surface energy of the substrate, expressed by γ or w_a , but also the elastic properties of the material and the geometry of the crack.¹³⁹ Nevertheless, quantitative prediction of the release force is rather difficult due to the complex interplay of the various properties of the

organisms and coatings.¹³⁶ In the case of a moving ship, forces are typically applied at an angle rather than in the normal direction to the elastomer surface. Thus, an additional component of interfacial slippage has to be considered.^{140,141}

4.1.1.2.2. Effect of the Elastic Modulus. According to the fracture mechanics equations already mentioned, the critical removal force was demonstrated to correlate far better with $(E\gamma_C)^{1/2}$ than with E or γ_C (Figure 16).¹¹⁶ The minimum of adhesion corresponds to the lowest value of elastic modulus but not to the lowest surface energy of the tested substrates (Table 4).¹¹⁶

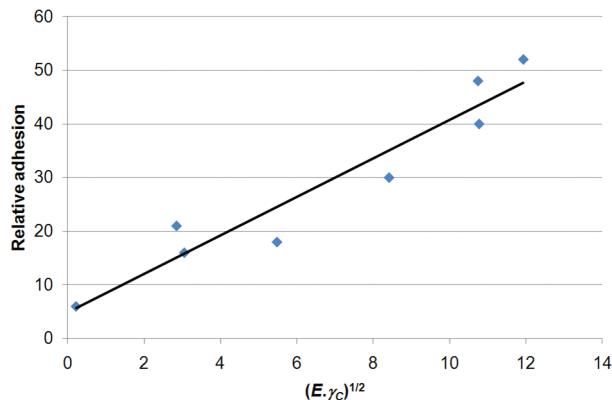


Figure 16. Relative adhesion (dimensionless) as a function of the square root of the product of critical surface energy (γ_C) and elastic modulus (E).

Table 4. Physical Properties of Some Polymers^a

polymer	relative adhesion	critical surface tension, γ_C (mN·m ⁻¹)	elastic modulus, E (MPa)	$(E\gamma_C)^{1/2}$
poly(hexafluoropropylene)	21	16.2	500	2.85
poly(tetrafluoroethylene)	16	18.6	500	3.05
poly(dimethylsiloxane)	6	23.0	2	0.21
poly(vinylidene fluoride)	18	25.0	1200	5.48
poly(ethylene)	30	33.7	2100	8.41
poly(styrene)	40	40.0	2900	10.77
poly(methyl methacrylate)	48	41.2	2800	10.74
Nylon 6-6	52	45.9	3100	11.93

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The mechanisms involved in preventing fouling differ between fluoropolymers and silicones. For the hard, glassy fluoropolymer coatings, because their surface is smooth and nonporous and exhibits low energy, a weak interface is formed with the marine adhesive. The high resistance of the surface to molecular interdiffusion and rearrangement gives a sharp, well-defined interface, which is easily snapped by an in-plane or out-of-plane shear mode. However, because the bulk modulus of fluoropolymers is higher than that of elastomers, the joint fails at higher critical stresses.¹³⁸ PDMS coatings generally have somewhat higher values of surface energy than fluoropolymers, and these materials likely form slightly stronger bonds with fouling organisms. However, due to the low modulus of the material, the application of a force to a foulant deforms the silicone, and a failure mode similar to peeling occurs. Therefore, this process requires less energy than detachment by shear or tension.^{138,142} Furthermore, a joint is considered tough if a

large amount of energy is expended to propagate a crack along it. Toughness of an interface depends mainly on the deformation of the adherends near the crack tip. As a crack moves along an interface, a polymer in the crack tip is placed under tensile stress. Newby et al.¹⁴⁰ showed that an adhesive slips on a PDMS surface toward the crack tip, reducing the extension of the polymer, thus reducing its tensile stress and reducing the energy needed to propagate the crack. This behavior does not occur on fluoropolymers or hydrocarbon polymers. Therefore, low bioadhesion coincides with low elastic modulus because the mobility of the low modulus surface allows the adhesive to slip during interfacial failure, reducing the energy input needed to achieve failure.¹¹⁷ The elastic modulus was shown to play an important role in the detachment of green alga *Ulva linza* from PDMS model coatings. A removal of 80% of sporelings was achieved at low moduli ($E = 0.2$ and 0.8 MPa) whereas almost no release was observed for the highest modulus ($E = 9.4$ MPa).¹⁴³ The release of pseudobarnacles (glued studs used as models of live barnacles, see section 4.1.1.3) in shear from platinum-cured silicones was reported to be favored as the coating modulus decreased from 1.3 to 0.08 MPa.¹⁴⁴

4.1.1.2.3. Effect of the Coating Thickness. The thickness is another characteristic of FRCs that plays an important role in the removal of foulants. Singer et al.¹³⁹ showed that the pull-off force, P_c , for removing pseudobarnacles from silicone varied in accordance with Kendall's model,¹³⁷ namely $P_c = f(t^{-1/2})$ for thin coatings (Figure 17), and that P_c was independent of coating thickness for thick coatings.^{116,139,145}

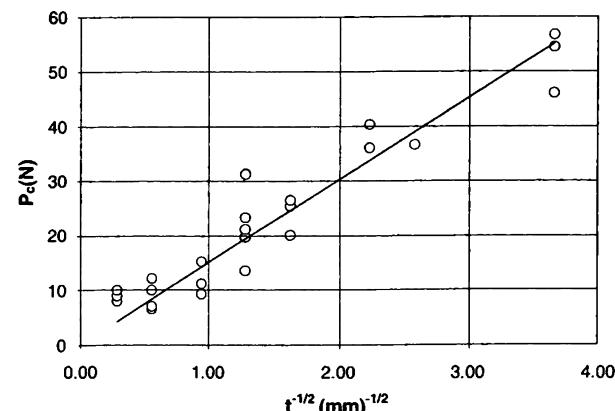


Figure 17. Pull-off force P_c vs $t^{-1/2}$ for pseudobarnacles on PDMS coatings. Reprinted with permission from ref 139. Copyright 2000 Taylor & Francis Group.

They also demonstrated that the pseudobarnacle release mechanism is dependent on the coating's thickness, t , and the contact diameter, a . The release mechanism was either by peeling for thick coatings ($a/t < 10$) or by void formation for thin coatings ($a/t > 10$).¹³⁹ In addition to these release mechanisms, a release mode known as fingering was also reported for other elastomer coating systems.¹⁴⁶ Mixed release modes were also observed for coatings with a thickness gradient.¹⁴⁷ Chaudhury et al.¹⁴³ studied the release of spores and sporelings of *Ulva linza* on PDMS coatings with thicknesses of 16, 100, and 430 μm . They showed that the release of sporelings was particularly improved for the 430- μm -thick coatings. In addition, the shear stress values for removal of pseudobarnacles from PDMS coatings was reported to increase

as the coating thickness decreased from 740 to 160 μm .¹⁴⁴ Like pseudobarnacle pull-off tests which verified the behavior predicted by Kendall's model,^{116,139,145} Wendt et al.¹⁴⁸ demonstrated that the critical removal stress of live barnacle *A. amphitrite* from silicone coatings was inversely proportional to the coating thickness, with average critical removal stress values of 0.093, 0.074, and 0.055 MPa on 0.1, 0.5, and 2 mm thick silicone coatings, respectively. However, several published reports using live animals (in contrast to pseudobarnacles) failed to find an inverse relationship between the coating thickness and pull-off force.^{139,149} The lack of a thickness dependence found by Singer et al.¹³⁹ was likely to be due to the fact that most of the barnacle basal plates broke during removal. In this case, the mechanics of detachment should not follow Kendall's model, which describes a fracture process where a basal plate would peel from an elastomer. It has also been found that, below $\approx 100 \mu\text{m}$ dry film thickness, barnacles can cut through to the underlying coating and thus establish strong adhesion. A thin film does not have the ability to absorb the cutting force from the edges of the barnacles as they attach to the surface, and once the coating has been penetrated down to the underlying hard primer, the adhesion of the barnacles increases greatly. As the barnacles subsequently continue to grow, their sharp edges further undercut the FRC, and in this way, the coating is forced up the sides of the barnacles.¹⁰⁸ Commercial FRCs are typically applied as duplex systems with a thickness of 150 μm for the silicone top-coat and 90 μm for the tie-coat. To determine the influence of both layer thicknesses on the FR properties, a model was developed which predicts a linear dependence between the pull-off force P_c required to remove pseudobarnacles and $(t^*)^{-1/2}$, where t^* is an effective top-coat thickness that takes into account the thicknesses and the bulk moduli of the top- and tie-coats.^{139,145}

4.1.1.3. Evaluation of Fouling Release Performances. The AF performances of biocide-based coatings are conventionally assessed through field static immersion tests by determining the type and abundance of micro-²⁶ and macro-organisms¹⁵⁰ attached on test panels. Evaluating performances of FRCs in such a way is not fully appropriated, as they are frequently fouled under static conditions. The effectiveness of such coatings is rather estimated by the strength of adhesion of settled fouling organisms. Several test methods have been developed to quantify fouling adhesion strength on FRCs. Among them, tensile and shear tests^{151–153} are employed for barnacles and other hard fouling organisms (e.g., oysters, tubeworms),^{154–156} and water jet tests^{152,157} as well as turbulent channel flow apparatus^{158,159} are used for soft micro-organisms and slime. Barnacles are ideal candidates, as they are found at most marine exposure sites and are able to settle on most substrates, including those with low surface energy. Moreover, their adhesion mechanism has been well studied.^{16,20,95,149,160–162} Barnacle adhesion is measured by dividing the tensile or shear force required to remove the barnacle by the surface area of the barnacle base plate. In an alternative to field tests, pseudobarnacles (epoxy-based studs) could be glued on the coating surface as models.^{116,144,145,155,163,164} Some limitations exist, as several features cannot be replicated with pseudobarnacles, such as the barnacle cement, which is substituted by synthetic glue,^{139,165} and the fact that live barnacles may show abnormal growth and/or cement production when attached to FRCs.^{20,148,149,166,167} Nevertheless, pseudobarnacles can give valuable comparative information together with a better understanding of the

adhesive failure mechanism if these limitations are understood.¹⁶⁸ The tensile method is still in use,^{165,168} but most recent studies have investigated FR performances under shear stress.^{148,151,153,169} Force gauges are usually employed for field testing following the standard procedure.^{152–155,164,170–172} The major advantages of the manual method are its cost, relative ease of use and portability, and thus its great utility for field measurements of adhesion strength of fouling organisms, for which it was developed.¹⁷³ Instruments that automate measurement of the force required to remove barnacles by shear stress have been introduced,^{148,163} but they do not automatically determine the critical removal stress, which requires that the removal force is normalized to the barnacle's basal area.^{151,153,154} This automated method has been developed as a technique for high-throughput screening of coatings in laboratories with live barnacles rather than for field measurements.¹⁷⁴ The main advantages of the automated method are the reduced time needed to test each barnacle and the ability to accurately test low numbers of smaller barnacles, with additional savings in time and manpower.¹⁷³ For silicone coatings, a barnacle adhesion strength lower than 0.02–0.20 MPa is usually measured by shear^{148,152,153,155,163,175–177} compared with Teflon (0.9 MPa)¹⁵² or epoxy- and urethane-based coatings (>1.5 MPa).^{58,152} Studies have been carried out to link laboratory data of attachment strength and fouling-release from a boat hull.^{103,178} Schultz et al.¹⁰³ proposed a model to correlate the measurements of the adhesion strength of barnacles and FR performance on a ship. This model, which relates barnacle adhesion strength to hydrodynamic drag forces generated by the movement of a ship, was used to predict the ship speed required for self-cleaning of individual barnacles. The authors correlated tensile and shear strength values applied on a barnacle plaque as a function of water velocity as shown in Figure 18. As an example, a vessel sailing at 7.7 m·s⁻¹ (15

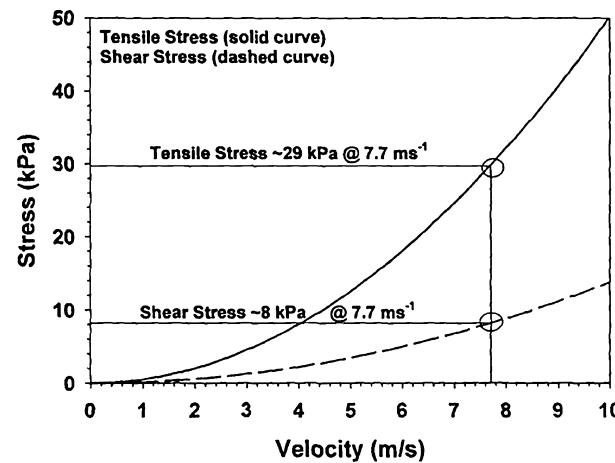


Figure 18. Variation in tensile and shear stresses with velocity: velocity for barnacle detachment due to tensile and shear stresses. Reprinted with permission from ref 103. Copyright 1999 Taylor & Francis Group.

knots) produces a tensile stress of 29 kPa and a shear stress of 8 kPa on a barnacle fixed on the hull. If the adhesion strength of a barnacle is less than the calculated tensile and shear stresses, it would be detached. This model predicted that, assuming free stream velocity and no boundary layer, the best-performing silicones would self-clean at about 10 knots.

In the case of soft, microfouling species such as algae and slime layers, tensile and shear tests are not suitable and hydrodynamic methods are more appropriate. Swain and Schultz¹⁵² developed a water jet test apparatus for field evaluations of test panels to determine the adhesion strength of soft and microfouling species. The original apparatus employed a hand-held nozzle to produce a controlled stream of water of known pressure. The pressure of the water jet is increased until all the fouling is removed or until the maximum pressure of the apparatus is achieved. Finlay et al.¹⁵⁷ developed a miniaturized and semiautomated version of this water jet method for reproducible evaluations, at laboratory-scale, of the short-term attachment strength of *Ulva linza* on microscope slides. More recently, an automated and miniaturized version of the water-jet apparatus has been developed for high throughput screening of potential AF and FR surfaces.¹⁷⁹ The adhesion strength of microfouling organisms may also be determined using turbulent water channel flow, which is more realistic for testing hull coatings than other flow cell designs, since surrounding boundary layers are turbulent in character.^{158,159} Flows of artificial seawater of up to $4.9 \text{ m}\cdot\text{s}^{-1}$ generate wall shear stresses of up to 56 Pa.¹⁸⁰ Schultz et al.¹⁵⁹ developed several models to correlate the adhesion strength of microfouling and the self-cleaning properties of a ship coated with FRCs.

4.1.2. Drag Reduction Ability. Any vessel propelled through the water has drag associated with it. In fluid dynamics, drag is defined as the force that opposes forward motion through the fluid and is parallel to the direction of the free-stream velocity of the fluid flow. Drag must be overcome by thrust to achieve forward motion. There are two types of drag: viscous drag, which predominates at low speeds and is largely determined by the frictional resistance caused by the surface roughness of a hull, and wave-making drag, which predominates at high speed and is determined by the length of the ship, and the ratio of the width to the vertical distance from the bottom of the hull to the waterline.¹⁸¹ For smooth, new ships, frictional resistance accounts for 80–85% of the total resistance in slow-speed vessels and as much as 50% in high speed vessels.^{47,49} Reducing drag resistance is important for ship-owners, as the resistance of a ship moving through water affects the ship performance and the fuel consumption as well as the gas emissions. There are several laboratory techniques for determining skin friction drag. These include rotating disks,¹⁸² rotating drums,^{181,183–185} or flow tunnels.^{186,187} Mirabedini et al.¹⁸¹ demonstrated that a silicone elastomer coating reduced skin frictional drag by 9–22%, at different velocities (6.5–22.7 knots), relative to other SPC coatings (Table 5). At higher velocities, the effect of coating type on the

frictional drag was found to be less important, as wave-making resistance has more effect on total resistance than skin frictional drag.

The main difference between FR and tin-free SPC systems lies in the texture characteristics, as shown in Figure 19.¹³² Whereas the tin-free SPC surface displays a spiky “closed” texture, the FR surface is characterized by a wavy “open” texture, implying that overall the surface is smoother.¹⁹

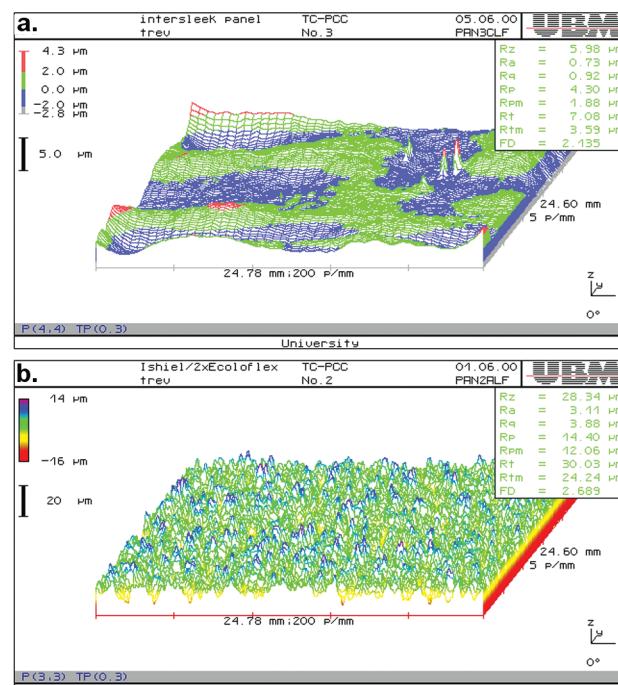


Figure 19. Profilograms of aluminum plates spray-coated with a FRC and a tin-free SPC surface. Reprinted with permission from ref 132. Copyright 2003 RINA.

- The “open” texture is characterized by a set of wavelength parameters (in the plane of the surface) including a lower mean absolute slope Δa ($\delta z/\delta x$), a lower mean absolute slope angle S_a , a higher average wavelength λ_a , and correlation length $\tau_{0.5}$.^{132,189} On the other hand, the surface roughness, which is perpendicular to the surface, is characterized by a set of height parameters, including the following:

- R_v , the maximum peak-to-valley height over the sample, the absolute value between the highest and lowest peaks.

- R_a , the average surface roughness, or average deviation, of all points from a plane fit to the test part surface.

- R_g , the root-mean-square deviation of all points from a plane fit to the test part surface.

- R_z , the ten-point height, or average absolute value of the five highest peaks and the five lowest valleys.

- Ku , kurtosis, a measure of the randomness of profile heights, and of the “sharpness” of a surface. A perfectly random surface has a value of three; the farther the result is from three, the less random and more repetitive the surface is. Spiky surfaces have a high value; bumpy surfaces have a low value.

- Sk , the skewness, a measure of symmetry of the profile about the mean line. Negative skew indicates a predominance of valleys, while positive skew indicates a “peaky” surface. Like Ku , Sk is a statistical descriptor that gives the average behavior of the surface height.

Table 5. Skin Friction Coefficient (Cf) and Drag Reduction (%) of a Silicone Elastomer Coating FRC with Respect to Different SPC Coatings at Various Reynolds Numbers^a

Re number ($\times 10^5$)	velocity (knot)	Cf FRC RTV-4511	Cf tin-based SPC coating	drag reduction of FRC (%)	Cf tin-free SPC coating	drag reduction of FRC (%)
2	6.5	0.263	0.337	22	0.333	21
3	10.4	0.221	0.261	17	0.268	17
6	18.2	0.197	0.226	13	0.231	15
8	24.7	0.180	0.197	9	0.204	12

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Surfaces are comprised of many “shapes”. The long wavelength shapes are assigned to “waviness” and the short wavelength features to “roughness”. The “cutoff wavelength” is the wavelength that separates roughness from waviness. The use of a single roughness parameter gives an incomplete representation of the concept of roughness, as two surfaces may have the same value of a height parameter and quite different waviness or texture. Weinell et al.¹⁸⁴ modeled the relationship between “macroroughness” (cutoff wavelength >50 mm), “microroughness” (cutoff wavelength <10 mm), and drag resistance. The authors found that for an ideal painted surface the coefficient attributable to microroughness was an order of magnitude higher than that attributable to macroroughness. The coefficient attributable to macroroughness had a negative sign at higher velocities, meaning that it had a decreasing effect on drag resistance as velocity increased. In addition to the coating type (i.e., FRC or SPC), it has been shown that the coating application technique has an effect on the drag resistance. Indeed, Candries and Atlar¹³² showed by measuring drag on coated surfaces in a rotor apparatus that applying a FR coating with a roller instead of spraying can increase the frictional resistance of the coating by around 2.5%.¹³² Compared to an uncoated PVC surface, the frictional resistance C_f increased on average by 4.3% for the sprayed FRC, by 5.7% for the rolled FRC, and by 8.0% for the sprayed SPC coating (Figure 20).¹³²

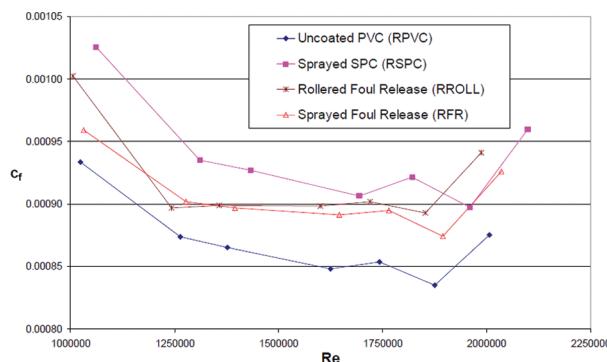


Figure 20. Local frictional resistance coefficients against Reynolds number for an uncoated PVC surface and surfaces coated with a sprayed SPC, rollered FRC, and sprayed FRC. Reprinted with permission from ref 132. Copyright 2003 RINA.

The application method for the FR coatings does not significantly affect the texture of the surface whereas the height parameters (R_a , R_q , R_t) are significantly changed (Table 6¹³² and Figure 21¹⁹). A rollered FR surface possesses a larger kurtosis value, due to the fact that large peaks occur much more

Table 6. Examples of Roughness Parameters of a Sprayed FRC Surface, a Rollerred FRC Surface, and a Sprayed (Tin-Free) SPC Surface¹³²

roughness parameter	sprayed FRC	rollered FRC	sprayed SPC
R_a (μm)	1.03	2.57	3.64
R_q (μm)	1.15	3.03	4.57
R_t (μm)	4.89	12.01	22.24
Sk	0.17	3.92	0.60
Ku	6.63	41.19	7.85
Δa (rad)	0.0063	0.0081	0.0493
Sa (deg)	0.36	0.46	2.82

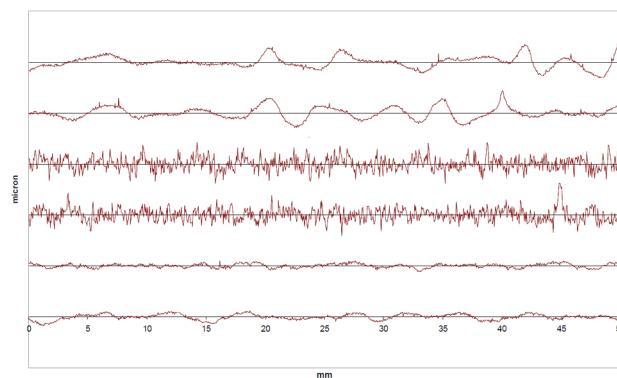


Figure 21. Pairs of typical roughness profiles of surfaces coated with (from bottom to top, respectively) a sprayed FRC, a sprayed SPC, and a rollerred FRC. The horizontal grid lines are separated by 25 μm . Reproduced from ref 19 by kind permission of the Institute of Marine Engineering, Science and Technology (IMarEST). Copyright 2003 IMarEST.

frequently on the rollerred FR surfaces. Candries and Atlar¹³² suggested that this greater number of high peaks present on a rollerred FRC may engender higher drag. The SPC surfaces display height parameters which are comparable to those for the rollerred FR surfaces, but the texture is significantly different from that for FR surfaces. Anderson et al.¹⁹ specified that the coating texture is dependent on the rheology of the paint (which is significantly different for FRC and SPC) whereas the amplitudes depend significantly on the application quality. However, a correlation analysis of the texture parameters with the amplitude parameters has shown that the two are interrelated. Consequently, poor applications can be expected to affect the texture parameter.¹⁹

The procedure adopted by the International Towing Tank Committee to correlate roughness with the added resistance of ships only accounts for a single roughness amplitude parameter: the average hull roughness (AHR), which is an average of R_{t50} (maximal R_t value over a distance of 50 mm).¹⁹⁰ However, as previously mentioned, the physical composition of a FR system is very different from those of tin-free SPC coatings, and the textures of both coatings are fundamentally different. Additional studies have demonstrated that a FRC even poorly applied with a higher R_{t50} value of 62 μm , compared with a SPC with $R_{t50} = 39 \mu\text{m}$, had 1.4% lower drag resistance than the SPC surface.¹⁰⁷ Candries and Atlar¹³² re-evaluate the correlation between roughness and drag for FRCs. They demonstrated that FRCs do not correlate with drag when they are characterized solely by a height parameter. They found a better correlation between roughness and drag when the coatings are characterized by $h = R_a \Delta a / 2$, a combination of the average height and mean absolute slope.¹³²

4.2. Chemical Structure and Formulation of Fouling Release Coatings

The next sections review the research into the synthesis of silicone-based and fluorinated polymers as candidate matrices of nontoxic FR marine coatings. The impact of the chemistry and the formulation on the FR performances of the corresponding coatings are discussed.

4.2.1. Silicone-Based Coatings. **4.2.1.1. Historical Use of Silicones as Marine Fouling Release Coatings.** The first results on the use of cross-linked silicones as marine coatings were patented by Robbart in 1961.⁵⁴ This invention was based

Table 7. Summary of Silicone-Containing Fouling Release Coatings

coating	coating characteristics	relative fouling resistance and fouling release performances	ref
unfilled hydrosilylation-cured PDMS coatings	–	control: RTV11 ↓ <i>B. eburneus</i> barnacle adhesion strength	176
SilasticT2	$\theta_W = 109 \pm 3.5^\circ$ $\gamma_S = 23 \pm 0.4 \text{ mJ}\cdot\text{m}^{-2}$ $E = 1.4 \text{ MPa}$	control: glass ↑ settlement of <i>Craspedostaurus</i> and <i>Amphora</i> diatoms similar settlement of <i>Navicula</i> cells ↑ adhesion strength of diatoms no removal of diatoms <i>Navicula</i> even at high shear stress for low E , ↓ pseudobarnacle adhesion strength when thickness ↑	41, 205 144
Pt-cured PDMS 160 and 740 μm -thick	$\theta_W = 118 \pm 2^\circ$ $\gamma_S = 18 \pm 2 \text{ mJ}\cdot\text{m}^{-2}$ $E = 0.08\text{--}1.30 \text{ MPa}$	for higher E , ↑ adhesion strength but less dependent on thickness at $E = 0.8 \text{ MPa}$, ↑ removal of <i>Ulva</i> spores and sporelings for the thickest coating (430 μm)	143
16-, 100-, and 430 μm -thick hydrosilylation-cured PDMS	$E = 0.2\text{--}9.4 \text{ MPa}$	at $t = 100 \mu\text{m}$, ↑ removal of <i>Ulva</i> sporelings with $E < 1 \text{ MPa}$ control: RTV11 ↓ barnacles adhesion strength: 0.048 MPa ($7 \pm 3 \text{ psi}$) instead of 0.082 MPa ($12 \pm 2 \text{ psi}$)	177
Pt-cured PDMS + trifunctional cross-linker	$\theta_{W,adv} = 108 \pm 3^\circ$ $\theta_{W,rec} = 90 \pm 4^\circ$	↓ <i>A. amphitrite</i> barnacles adhesion strength when thickness ↑ from 0.1 to 2 mm ↓ pseudobarnacles adhesion strength for coatings with lower filler content (lower tensile strength)	148 163
hydrosilylation-cured PDMS PDMSdp125	–	no significant effect of cross-link density on adhesion strength ↓ pseudobarnacles adhesion strength for coatings with lower filler content (lower tensile strength)	163
condensation cured PDMS with 0–29 wt % CaCO_3	$\gamma_C = 22\text{--}23 \text{ mN}\cdot\text{m}^{-1}$ 0.298–0.544 (storage modulus) $\gamma_C = 22\text{--}23 \text{ mN}\cdot\text{m}^{-1}$ 0.036–0.386 (storage modulus)	no significant effect of cross-link density on adhesion strength negligible effect of filler loading on γ_C ↓ adhesion strength of <i>B. eburneus</i> barnacles and <i>Ostrea</i> sp. oysters for CaCO_3 -filled coating the interaction of silicone oil type and filler type influences the adhesion strength of marine organisms control: SilasticT2	170 89
hydrosilylation-cured PDMS with 5–16 wt % filler and different cross-linking density	–	similar (higher) <i>Ulva</i> spores settlement and release for the 50cSt (5000cSt)-oil modified ↓ modulus with increased oil amount	155
SiO_2 or CaCO_3 -filled condensation-cured PDMS with different types of silicone oils	–	control: RTV11 ↓ total fouling coverage ↓ adhesion strength of barnacles (0.041 MPa instead of 0.069 MPa) similar adhesion strength for oysters, tubeworms, slime, and soft fouling limited ↑ of γ_S^P after immersion in seawater ↓ in abrasion resistance only 1.1 wt % of oil leached out after 12 months in salt water	156
SilasticT2 + PDMS oil (5 wt % 50cSt PDMS, 20 wt % 50cSt PDMS, 5 wt % 5000cSt PDMS)	$\gamma_C = 22.4 \pm 1.3 \text{ mN}\cdot\text{m}^{-1}$	control: RTV11 similar total fouling coverage ↓ barnacles and oyster adhesion strength in Florida no significant effect on oysters and tubeworms adhesion in Hawaii no change in adhesion strength over time, whereas it increased for free-oil RTV11 control: Teflon and epoxy coating ↓ barnacle adhesion strength for silicone coatings (0.06–0.11 MPa) compared with Teflon (0.88 MPa) and Epoxy (2.23 MPa) ↓ slime adhesion strength for silicone coatings using oil, with better properties over time for methyl phenyl silicone fluid	152 175
RTV11+ 10 wt % PDMDPhS oil	$\gamma_C = 22.1 \text{ mN}\cdot\text{m}^{-1}$ $\gamma_S = 27.5 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^P = 4.3 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^D = 23.2 \text{ mJ}\cdot\text{m}^{-2}$ $E = 1.19 \text{ MPa}$	control: RTV11 similar total fouling coverage ↓ barnacles and oyster adhesion strength in Florida no significant effect on oysters and tubeworms adhesion in Hawaii no change in adhesion strength over time, whereas it increased for free-oil RTV11 control: Teflon and epoxy coating ↓ barnacle adhesion strength for silicone coatings (0.06–0.11 MPa) compared with Teflon (0.88 MPa) and Epoxy (2.23 MPa) ↓ slime adhesion strength for silicone coatings using oil, with better properties over time for methyl phenyl silicone fluid	152 175
RTV11+ 10 wt % PDMDPhS oil	–	control: RTV11 similar total fouling coverage ↓ barnacles and oyster adhesion strength in Florida no significant effect on oysters and tubeworms adhesion in Hawaii no change in adhesion strength over time, whereas it increased for free-oil RTV11 control: Teflon and epoxy coating ↓ barnacle adhesion strength for silicone coatings (0.06–0.11 MPa) compared with Teflon (0.88 MPa) and Epoxy (2.23 MPa) ↓ slime adhesion strength for silicone coatings using oil, with better properties over time for methyl phenyl silicone fluid	152 175
silicone + methyl phenyl silicone fluid	$\gamma_C = 22 \text{ mN}\cdot\text{m}^{-1}$	control: Teflon and epoxy coating ↓ barnacle adhesion strength for silicone coatings (0.06–0.11 MPa) compared with Teflon (0.88 MPa) and Epoxy (2.23 MPa) ↓ slime adhesion strength for silicone coatings using oil, with better properties over time for methyl phenyl silicone fluid	152
silicone + organic modified polysiloxane	$\gamma_C = 22 \text{ mN}\cdot\text{m}^{-1}$	control: intershield (epoxy coating) ↓ barnacle adhesion (0.11–0.29 MPa), 20 times lower than Intershield	175
RTV3140 (silicone)	$\gamma_C = 25 \text{ mN}\cdot\text{m}^{-1}$	control: intershield (epoxy coating) ↓ barnacle adhesion (0.11–0.29 MPa), 20 times lower than Intershield	175
Intersleek (International Paint)	$\gamma_S = 19.4 \pm 1.2 \text{ mJ}\cdot\text{m}^{-2}$	control: intershield (epoxy coating) ↓ barnacle adhesion (0.11–0.29 MPa), 20 times lower than Intershield	175
Everclean (NOF)	$\gamma_S = 21.3 \pm 1.3 \text{ mJ}\cdot\text{m}^{-2}$	γ_S ↑ after 6 months immersion	26
Bioclean (Chugoku)	$\gamma_S = 19.9 \pm 0.7 \text{ mJ}\cdot\text{m}^{-2}$	control: TBT-SPC, Cu-SPC, Cu-Ablative	26
Biox (Kansai Paint)	$\gamma_S = 37.2 \pm 2.9 \text{ mJ}\cdot\text{m}^{-2}$	control: TBT-SPC, Cu-SPC, Cu-Ablative	26

Table 7. continued

coating	coating characteristics	relative fouling resistance and fouling release performances	ref
Biox L (Kansai Paint)	—	similar bacteria and diatoms settlement after static immersion, ↑ removal after dynamic immersion (except for diatom compared to Cu-Ablative)	
2–3 mm thick Sylgard184	—	control: PMMA	178
Veridian (International Paint)	—	↑ removal of cyprids and juvenile barnacles	
Veridian (International Paint)	—	better FR properties for Veridian compared to Sylgard184 control: glass	159
	—	similar settlement and ↑ removal of <i>Ulva</i> sporelings	

on the discovery that the settlement of barnacles could be largely avoided with a surface coating composed of a silicone resin. Krøyer¹⁹¹ found in 1970 that a cured silicone rubber coating showed a lower density of fouling in comparison to a silicone resin after one month of seawater immersion. In addition, the removal of organisms adhered to the coated surface required less energy. The silicone rubber was differentiated from silicone resin in that silicone resins were highly cross-linked siloxane structures. Therefore, a coating which consists of relatively soft silicone rubber is more efficient than a hard smooth silicone resin layer. In addition, Mueller and Nowacki¹⁹² reported the use of cured silicone rubber or elastomer as nontoxic AF and drag reducing coatings for vessels moving through the water. In 1977, Milne¹⁹³ first patented the use of silicone oil (i.e., poly(methylphenylsiloxane)) within a cured silicone rubber to enhance the AF efficiency of *in situ* immersed coated panels. Due to the success of TBT-SPC systems, the commercialization of silicone elastomers as FRCs was delayed until the 1980s, when the environmental problems associated with TBT-SPC antifouling were starting to appear.¹⁹ An overview of the types of silicone elastomers with FR properties investigated so far is provided in Table 7.

4.2.1.2. Chemistry of Silicone Fouling Release Coatings. FRCs are mainly composed of silicone elastomers which consist of organic and inorganic groups. The backbone is made up of alternating silicon and oxygen atoms. Each silicon atom is linked to two organic groups, while the chain-end silicon atoms have a third group, which could be a hydroxyl, amino, or alkoxy substituent. In the most common silicone elastomer, PDMS, the side groups are methyl groups, as illustrated in Figure 22.

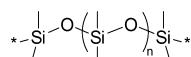


Figure 22. Chemical structure of a PDMS backbone.

To ensure a proper film formation, the silicone polymers have to be cross-linked. For evident practical reasons, the most

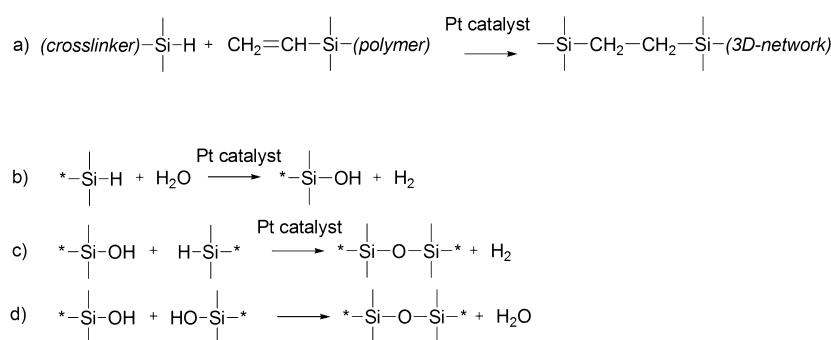
desirable cross-linking method is a room temperature vulcanized-type that can be formulated and applied as coatings onto large structures such as ships.¹⁹⁴ The silicone chemistry used for marine FRCs is based on two well-known curing reactions¹⁹⁵: (i) the hydrosilylation reaction and (ii) the condensation reaction. The hydrosilylation reaction occurs between two precursors of polysiloxane type: one comprising vinyl end-groups and the other bearing hydrosilane groups, which act as cross-linkers (Scheme 2).¹⁹⁶

Platinum catalysts such as chloroplatinic acid (H_2PtCl_6) are typically used in hydrosilylation reactions.¹⁹⁷ Secondary reactions, referred to as postcure reactions, may also occur and are especially favored with an excess of cross-linker with a potential release of H_2 gas. In such addition cure systems, the surface of hydrophilic fillers have to be treated so that water and SiOH contents are minimal in order to prevent such secondary reactions. Other drawbacks come from the potential toxicity of the catalyst used in hydrosilylation, and cleanliness is absolutely necessary. In addition, many olefinic compounds can act as inhibitors for hydrosilylation, and they have to be excluded.¹⁷⁶

Condensation cure systems are also commonly used to produce silicone elastomers. The condensation reaction occurs between a precursor of polysiloxane type comprising silanol end-groups and a cross-linker resulting in siloxane (Si-O-Si) bonds and the release of a volatile leaving group. The main reactions involved in the condensation cure are represented in Scheme 3.

The cross-linkers and catalysts often employed in condensation-cured FRCs are reported in Table 8. Although very effective, most often colorless, liquid, and soluble in silicone oils, the tin-based catalysts have been reported as toxicants. Recent studies found in the patented literature proposed new tin-free catalysts for cross-linkable FR silicone elastomers for marine applications, including zinc-based catalysts (e.g., zinc bis(2,2,7-trimethyl-3,5-octanedionate) 20¹⁹⁸), as well as metal-free catalysts based on silylated tri- or tetrasubstituted guanidines (e.g., 2,3-dicyclohexyl-1-methyl-1-(3-(trimethoxysil-

Scheme 2. Pt-Catalyzed Addition Cure: (a) Hydrosilylation; (b–d) Side Reactions



Scheme 3. Simplified View of the Reactions Involved in the Condensation Curing of PDMS Using an Alkoxy silane as Cross-Linker: (a) Cross-Linker Hydrolysis; (b) Secondary Condensation Reaction; (c) Network Formation from Silanol-Terminated PDMS and Cross-Linker; and (d) Reaction of Silanol-Terminated PDMS with Silanol Sites Generated by Reaction a

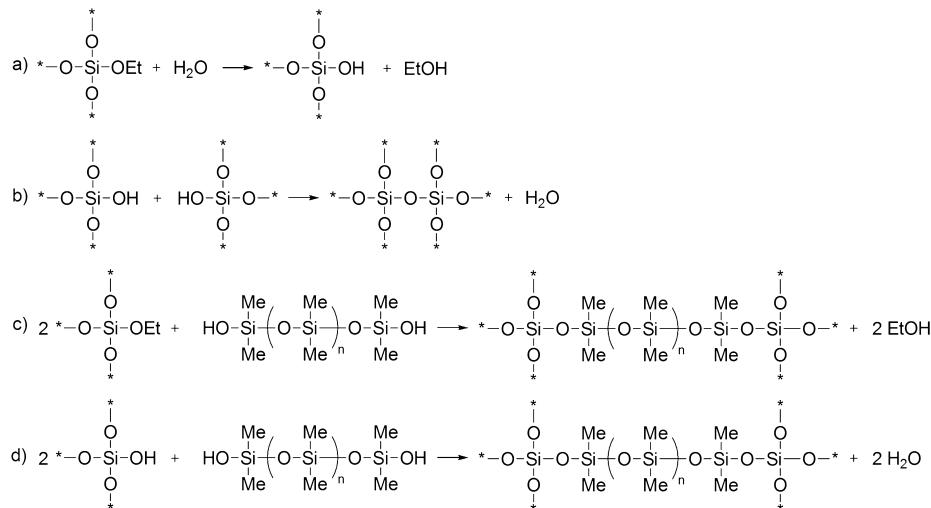


Table 8. Cross-linkers and Catalysts Typically Used in Condensation Cured Silicone FRCs (See Chart 2)

function	product	CAS number
cross-linker	tetraethoxysilane (TEOS) 13	78-10-4
cross-linker	tetrapropoxy silane 14	682-01-9
cross-linker	ethyl polysilicate 15	11099-06-2
catalyst	dibutyltin dilaurate 16	77-58-7
catalyst	diocetyl tin dilaurate 17	3648-18-8
catalyst	dibutyl dimethox stannane 18	1067-55-6
catalyst	dibutyltin diacetate 19	1067-33-0

yl)propyl)guanidine **21**¹⁹⁹) or nonsilylated molecules (e.g., 1-butyl-2,3-dicyclohexyl-1-methylguanidine **22**²⁰⁰).

One advantage of condensation cure chemistry is that network formation occurs over a wide range of stoichiometries, as cross-linker species in excess of that required for condensation with PDMS precursor undergo self-condensation (Scheme 3b) to produce a siliceous phase.¹⁷⁶ The resulting

network has a more complex structure compared to those of networks generated by hydrosilylation.¹⁷⁶ Another practical difference between hydrosilylation and condensation cures is the kinetics of the cure. Hydrosilylation cures require an induction period (usually 5–10 min) followed by rapid gelation and network formation, whereas condensation cures, with TEOS **13** as cross-linker and dibutyltin dilaurate **16** as catalyst, occur gradually, with thickening, gelation, and tack-free film formation within a few hours. With ambient humidity higher than 30%, hydrolysis is complete within 24 h. If optimum chemical stability (mass loss in water) is a criterion, complete cure takes 2–3 weeks. The network formation will not cure in dry air, while humidity is not a variable in hydrosilylation curing.¹⁷⁶

Three commercially available PDMS elastomers are commonly used as standard silicone FRCs in the literature (Table 9). Sylgard184 (Dow Corning) is an unfilled, clear two-part PDMS-based formulation containing an α,ω -vinyl

Chart 2. Cross-linkers and Catalysts Typically Used in Condensation Cure Silicone FRCs

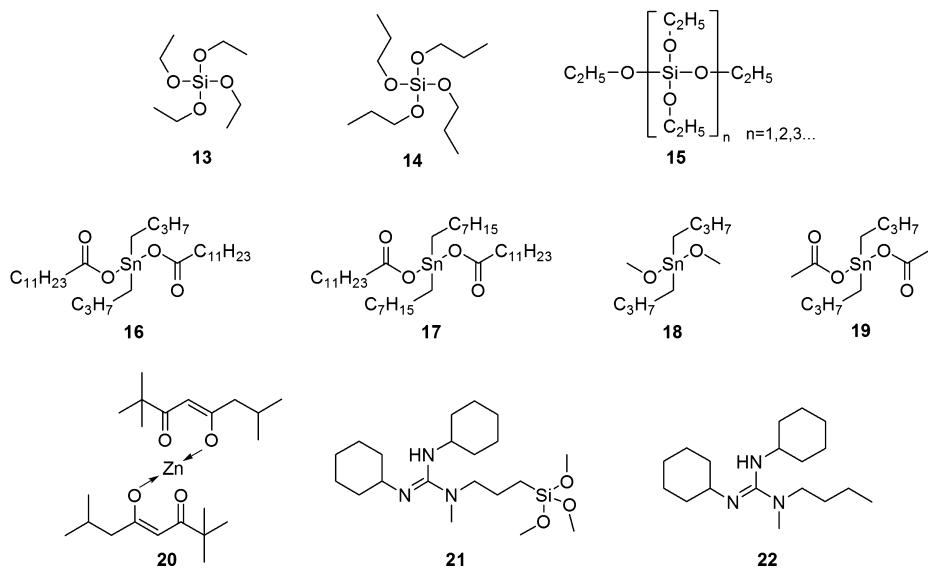


Table 9. Characteristics of Typical PDMS Elastomers Used as FRC Models

	unfilled hydrosilylation cured silicone	filled condensation cured silicone	
	Sylgard184	SilasticT2	RTV11
θ_W (deg)	101, ¹⁷⁴ 106 ²⁰⁷	109.1 \pm 3.5, ²⁰⁵ 112 ⁴¹ \pm 3, ⁸⁹ 109 \pm 3.5 ⁴¹	100 ²⁰⁷
$\theta_{W,adv}$ (deg)	110 ²⁰⁷	115.1 \pm 3.8 ⁸⁹	103 ²⁰⁷
$\theta_{W,rec}$ (deg)	80 ²⁰⁷	68.7 \pm 2.2 ⁸⁹	94 ²⁰⁷
$\Delta\theta$ (deg)	30 ²⁰⁷	46.4 \pm 1.7 ⁸⁹	9 ²⁰⁷
γ_C (mN·m ⁻¹)		23.0 \pm 0.4 ²⁰⁵	22.9 ¹⁵⁵
γ_S (mJ·m ⁻²)		21.5 \pm 1.8 ⁸⁹	25.1 ¹⁵⁵
γ_S^P (mJ·m ⁻²)			2.4 ¹⁵⁵
γ_S^D (mJ·m ⁻²)			22.7 ¹⁵⁵
E (MPa)	2.6 \pm 0.2, ¹⁷⁴ 0.96–1, ²⁰⁷ 3 ¹³⁹	1.3, ²⁰⁸ 1.43 ²⁰⁵	1.8 \pm 0.4, ²⁰⁶ 1.4, ²⁰⁹ 1.56, ²⁰⁷ 1.44 ¹⁵⁵

terminated poly(dimethylsiloxane) polymer, a poly(dimethylsiloxane-co-hydrogenomethylsiloxane) copolymer, a vinyl resin additive, and a platinum-based catalyst.²⁰¹ SilasticT-2 (Dow Corning) is another commercial PDMS elastomer often used as a standard due to its FR efficiency against barnacles and *Ulva* alga.^{202,203} This transparent two-part coating is cured by platinum-catalyzed hydrosilylation from a mixture of the base resin to curing agent. RTV11 (General Electric) is a representative condensation-cured silicone elastomer. This PDMS elastomer is formulated as a two-part system, containing 60–80 wt % of hydroxy-terminated PDMS ($M_w = 26,000$ g·mol⁻¹), 32 wt % of CaCO₃ filler, 1.9–2.1 wt % of ethyl silicate 40 (ES40) cross-linker, and dibutyltin dilaurate catalyst 16.²⁰⁴ ES40, with the approximate empirical formula Si(O)(OEt)₂, contains Si(OEt)₄ (TEOS, 13) and oligomeric and cyclic ethoxysiloxanes. When TEOS 13 is used alone to generate coatings, evaporative loss is high (up to 90%) and unpredictable. ES40, which is comprised mostly of higher molecular weight ethoxysiloxanes, has much lower volatility. Furthermore, the quantity of volatile organics (ethanol) evolved during curing is half that of TEOS 13.¹⁷⁶ These three PDMS elastomers are characterized by a high water CA, a low critical surface energy, and low elastic modulus values.^{41,89,139,155,174,205–209}

These fundamental properties of PDMS elastomers are related to the specific characteristics of the siloxane bonds,²¹⁰ that is the combination of a flexible backbone and low surface energy side groups. The siloxane backbone has a unique flexibility which results from several parameters, including the Si–O bond length (1.65 Å), the flat siloxane bond angles (159°), the partially ionic (nondirectional) nature of the bond, and an alternating divalent group in the backbone yielding increased spacing between corresponding Si substituent groups (2.99 Å).¹⁷ PDMS with a glass transition temperature T_g of –127 °C has the most flexible backbone among the common polymers. As a result, it can readily adopt the lowest surface energy configuration through a close packing of the pendant methyl groups at the PDMS/air interface. In addition, the molecular weight of the silicone precursor and the cross-link density within the elastomeric network influence the elastic modulus and the toughness of the resulting FRC.

4.2.1.3. Influence of the Formulation on the Fouling Release Properties. The formulation of silicone-based FRCs uses similar principles to those used for other coatings, even

though there is an even more critical focus on maintaining the specific properties of the silicone matrix (i.e., low surface energy and elastic modulus) throughout their service life. Any loss of one of them will irreversibly trigger the fouling process. Like most paints, FRCs are formulated with fillers (e.g., calcium carbonate (CaCO₃) and silica (SiO₂)) as well as pigments which provide opacity and color (e.g., titanium dioxide (TiO₂), iron oxides, carbon black, etc.). Calcium carbonate is often used as an extending filler to reduce the cost of the silicone elastomers. CaCO₃-based FRCs were shown to exhibit a mass loss when immersed in water due to the dissolution of CaCO₃ at the near-surface.¹⁷⁷ This CaCO₃-depleted layer displayed a lower elastic modulus than the coating bulk, which may improve the FR properties, although this may be offset by the negative effect of increased roughness.^{176,204} However, Dalton et al.²¹¹ suggested that exposure of CaCO₃ at the surface could assist bacterial colonization with a resultant increase in fouling. Fumed silica is also a typical high-surface-area filler incorporated in FRCs to provide strength.²¹² The surface silanol groups interact with the siloxane bonds through hydrogen bonding (Figure 23) and create a mechanical

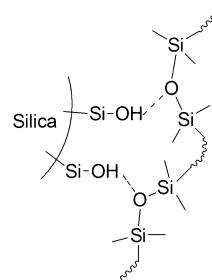


Figure 23. Hydrogen interactions between silica fillers and PDMS.

reinforcement. In condensation-cured PDMS, they also react with the cross-linkers forming a covalent bond.¹⁹⁶ The tensile strength of a nonfilled, cross-linked PDMS initially at *ca.* 0.14 MPa (20 psi) has been shown to increase 30-fold upon the addition of 15 wt % of SiO₂ fillers at a value of more than 4 MPa (600 psi).¹⁹⁶ Pseudobarnacle adhesion strength values were shown to increase from 0.09 to 0.21 MPa as the filler loading increased from 0 to 29 wt %, whatever the filler type (SiO₂ or CaCO₃).¹⁶³ This increase in filler loading did not have an appreciable effect on critical surface tension and surface roughness; however, as the filler loading increased, the tensile strength of the coating also increased. Therefore, coatings with the greatest durability and strength will be the least effective in terms of easy removal of fouling organisms. In condensation-cured PDMS, pretreated SiO₂ fillers could be used (i.e., hydrophobic SiO₂), as they could be more easily dispersed in PDMS and have lower moisture content but provide lower reinforcement.¹⁹⁶

The addition of pigments such as TiO₂ was demonstrated to affect both the mechanical and adhesion properties of a condensation-cured silicone elastomer coating.²¹³ An increase of the mechanical properties, including tensile strength, elastic modulus, abrasion resistance, and energy to break the coating, was only observed up to 15 wt % of TiO₂ content. In addition, pull-off tests revealed that the adhesion strength of the coating on the underlying tie-coat and epoxy primer increased with increasing the pigment level up to 10 wt %. This was attributed to an increase of the cohesive strength and modulus of the coating. However, further increase of the pigment reduced the

adhesion strength due to pigment aggregation and difficulty of pigment dispersion at higher solid contents. FRC paints may also contain additive oils (1–10 wt %) which were reported to act as softeners (reduced friction, higher flexibility) and to improve the FR performance.^{89,155,164} In 1977, Milne¹⁹³ first demonstrated that the use of poly(methylphenylsiloxane) fluid within a condensation-cured polysiloxane elastomer enhanced the AF efficiency of *in situ* immersed coated panels. Carboxyl-functionalized organosilicon polymers were also incorporated in PDMS elastomers to improve their FR properties.²¹⁴ Several other inventors reported the use of silicone-free oils such as low-molecular weight polyisobutylene,²¹⁵ liquid paraffin-petrolatum, perfluorinated polymers, or oligomers²¹⁶ as FR promoters. These nonreactive additive oils (i.e., they do not take part in the network formation) are able to migrate to the surface of the cured coating.²¹⁷ This diffusion effect could be enhanced by the volume shrinkage due to the cross-linking reaction,²¹⁸ the incompatibility of the oil with the silicone network, and its high flexibility. It has been postulated that the surface structure of silicone FRCs could change when the nonbonded oils migrate to the coating surface, allowing a detachment of fouling organisms by slippage.¹⁴⁰ In other words, fouling organisms settle on the oil rather than on the surface of the coating. The joint between oil and coating is weak and easily breaks off; then oil, taking early stages of fouling with it, is released into the sea.¹⁹⁶ Incorporation of silicone oils into the coatings was investigated in the range of 0–20 wt % by Edwards et al.²¹⁹ The results suggested that silicone oil had a significant positive effect on the enhancement of the *in situ* AF performance if high concentrations were used (between 10 and 20 wt %), and the enhancement was assumed to rely on the formation of a surface film. In addition, elutable components, such as oils added to a tougher silicone coating matrix, can extend coating efficiency and longevity.^{163,164} Truby et al.¹⁵⁵ showed that the adhesion strength of barnacles is decreased from 0.069 to 0.041 MPa on RTV11 PDMS coatings incorporating 10 wt % of nonbonded poly(dimethyldiphenylsiloxane) (PDMDPhS) oils compared to pure PDMS with only moderate decreases in the elastic modulus of the coatings. However, these results were not observed for oysters or tubeworms and the incorporation of oil did not significantly affect the water jet adhesion strength of adherent slime and soft fouling organisms. In a similar study, the incorporation of a PDMDPhS oil into RTV11 decreased the adhesion strength of barnacles *B. eberneus* (0.043 MPa instead of 0.067 MPa without oil) and oysters (0.060 instead of 0.103 MPa) whereas it did not impact the adhesion strength of tubeworms. While the adhesion strength of tubeworms on the RTV11 coating without free oil increased over time, there was no significant change in adhesion strength of hard fouling organisms over time on oil-containing RTV11 coatings. Stein et al.¹⁷⁰ studied the effect on FR performance of combined factors, i.e. oil and coating type (CaCO_3 or SiO_2 filler) in condensation-cured PDMS elastomers. They reported that not all oils exhibited the same performance benefit and the overall efficiency was a function of oil functionality, coating type, and the interaction of the oil with the coating. The diffusion of additives oils may be controlled by using oils which are more compatible with the silicone elastomer²²⁰ or are reactive,²²¹ whereby the fluid could leach out constantly of the cross-linked matrix over many months.

4.2.1.4. Promoting Adhesion of Silicone Fouling Release Coatings. While silicone elastomers are recognized as effective FRCs, they suffer from poor adhesion when they are directly

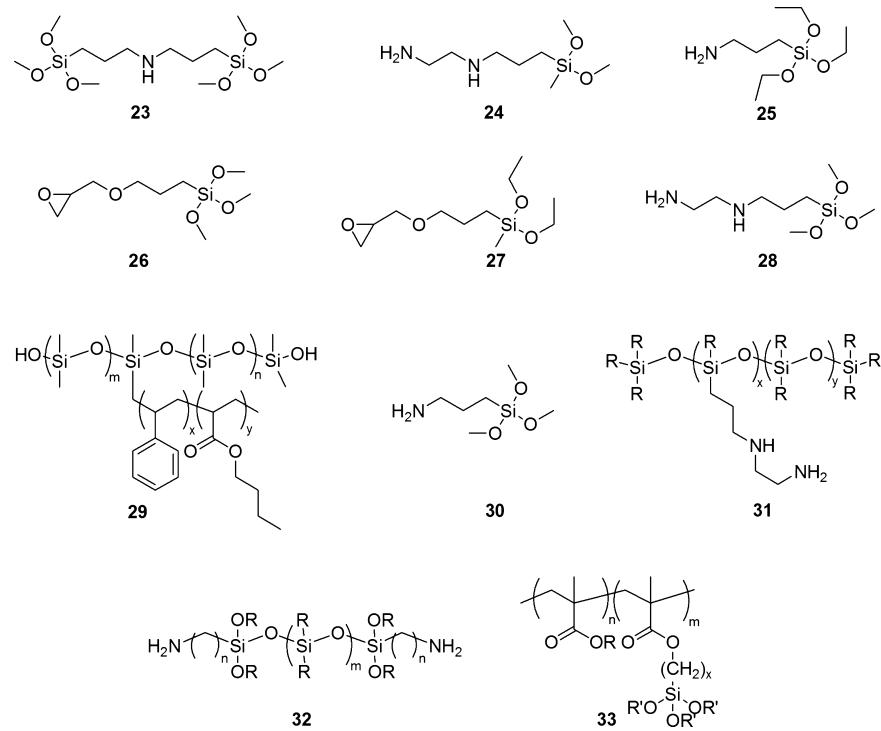
applied on underlying substrates, such as anticorrosive epoxy resins used on ship hulls. It has been shown that epoxy coatings have critical surface tension values between 30 and 37 $\text{mN}\cdot\text{m}^{-1}$.²²² A higher surface energy and acidic component of the surface energy of this sublayer are required to yield the highest adhesion with the silicone-based upper layer. The adhesion strength of the PDMS top-coat to the underlying substrate can be improved by various methods including mechanical alteration of the surface or establishing polar interactions or chemical bonding through the use of a bonding agent (also known as an adhesion promoter) or the use of an intermediate layer (also called tie-layer or tie-coat). The adhesion promoters could be added directly in the epoxy-based anticorrosive underlayer,²¹² in the silicone rubber top-coat,^{223,224} or in the tie-coat.^{212,225–229} It was usually shown that these compounds contain functionalities including alkoxy, epoxy, and amino residues which are susceptible to reacting with both the silicone and the epoxy-based layers (Table 10).

Table 10. Characteristics of Tie-Coats and Adhesion Promoters in FR Systems (See Chart 3)

tie-coats	chemical structure of adhesion promoters	refs
—	bis-(γ -trimethoxysilylpropyl)amine 23 N-beta-(aminoethyl)- γ -aminopropyl methyldimethoxysilane 24	229
amino-functionalized polysiloxane, hydroxyl-functionalized PDMS, epoxy-functionalized PDMS	γ -aminopropyltriethoxysilane 25 γ -glycidoxypolypropyltrimethoxysilane 26 γ -glycidoxypropylmethyldiethoxysilane 27	225
hydroxyl-functionalized PDMS	γ -glycidoxypolypropyltrimethoxysilane 26	
condensation-cured silicone-based and chlorinated polyethylene	bis(trialkoxysilylalkyl)amines N,N'-bis(trialkoxysilylalkyl) alkylenediamines alkoxy silane N-(2-aminoethyl)-3-aminopropyl trimethoxysilane 28	226
moisture-curable PDMS grafted copolymer 29	—	231, 232
blend of epoxy paint with a silicone condensation cure catalyst system	γ -aminopropyltrimethoxysilane 30	228, 234
moisture curable PDMS grafted copolymer 29	amino-functionalized polysiloxane 31	212, 227
trialkoxysilylalkyl methacrylate-based copolymer 33	α,ω -diamino-functionalized polysiloxane fluid 32	235

Esfandeh et al.²²⁹ investigated various silane-based adhesion promoters with the general chemical formula R-Si(OR')₃. These organosilanes were mixed with the epoxy resin or the silicone rubber, or a mixture of both of them, to developed new tie-coats for a silicone rubber upper layer. Higher adhesion strength values were demonstrated for the tie-coat made of the bis(γ -trimethoxysilylpropyl)amine 23 together with a 70/30 or 50/50 mixture of the PDMS silicone rubber and the epoxy resin. γ -Glycidoxalkylalkoxysilanes such as γ -glycidoxypolypropyltrimethoxysilane 26 or γ -glycidoxypropylmethyldiethoxysilane 27 were also used as adhesion promoters in a three-part patented tie-coat.²²⁵ Specific tie-coats were investigated to obtain duplex systems, with the most investigated one being moisture-curable PDMS grafted with a copolymer 29

Chart 3. Tie-coats and Adhesion Promoters in FR Systems.



containing butyl acrylate and styrene monomer units. The synthesis of this thermoplastic elastomeric formula was first patented in 1973,²³⁰ and its use was reported in several other patents^{212,227,231–233} and scientific papers^{139,164,170,207} under the trade name Silgan J501. Harblin²³⁴ reported that this silicone-organic tie-coat exhibits good adhesion with a silicone top-coat such as RTV11, while poor adhesion was observed with the epoxy underlayer. Therefore, a tie-layer was developed using a blend of an epoxy paint with a room temperature vulcanizable silicone condensation cure catalyst system and γ -aminopropyltrimethoxysilane **30** as adhesion promoter. In addition, the incorporation of an amino-functionalized polysiloxane **31** or α,ω -diamino-functionalized polysiloxane **32** fluid in the Silgan J501 tie-coat was suggested by Carroll et al.²¹² This curable grafted copolymer was also incorporated directly into an anticorrosive paint²²⁷ or into the PDMS top-coat.²³³ The latter case provides a monoplex system that self-assembled once applied, i.e. the top-coat components rose toward the surface and the tie-coat components moved down toward the underlying epoxy coating. This monoplex system does not have well-defined layers, in contrast to silicone-based duplex systems.

Poly(methacrylate) chains bearing trialkoxysilylalkyl groups **33** could be added to the underlying coating to enhance its adhesion properties with an upper layer of curable PDMS-based polymer containing hydroxyl-terminated groups. The trialkoxysilyl groups are thus able to react with the hydroxyl groups through condensation reactions.²³⁵

4.2.2. Fluorine-Based Coatings. **4.2.2.1. Historical Use of Fluoropolymers as Fouling Release Coatings.** Fluoropolymers are well-known for their nonpolar nature, which confers a hydrophobic character to their surfaces and a very low critical surface tension or surface energy in the range of 10–20 mN·m⁻¹. Zisman¹²⁴ established that surface energies depend on the chemical moieties and decrease in this order: -CH₂ (36

mN·m⁻¹) > -CH₃ (30 mN·m⁻¹) > -CF₂ (23 mN·m⁻¹) > -CF₃ (15 mN·m⁻¹). The first use of fluoropolymers as FRCs was patented by Berque²³⁶ in 1973, with the use of fluoropolymers such as poly(tetrafluoroethylene) PTFE or fluorinated ethylene-propylene copolymers for undersea protection of ship hulls. Because PTFE is completely insoluble in common organic solvents, the application process implied the projection of powder or emulsion on heated substrates. In the 1970s, highly fluorinated epoxy and polyurethane coatings were investigated by Griffith's group.²³⁷ A PTFE-filled fluorinated polyurethane paint was tested on a harbor tugboat called SeaMule and was regularly inspected and cleaned over a period of 13 years. The material was unique in that it provided a surface with approximately the same coefficient of friction as Teflon, was hydrophobic, was UV resistant, and at the same time provided an abrasion resistance four times that of Teflon. The coating was easily cleaned but suffered from damages caused by the sharp shell edges of barnacles which roughened the surface, and therefore, mature barnacles could adhere to the uneven paints with high strength, preventing easy removal. This capacity of barnacles to strongly adhere to fluorinated surfaces, despite their low surface energy, was attributed to a high localized polarity of the carbon-fluorine bond, which allows very polar groups in barnacle cement to develop a close association over time.²³⁸ PTFE, which was initially considered as a promising FR or nonstick candidate because of its low surface energy, was shown to rapidly accumulate biofouling because irregularities on the surface enable bioadhesives to invade and cure in microcavities and create secure mechanical interlock.²³⁹

The following research areas developed in the patent and scientific literature were based on the development of fluoropolymer coatings containing fluorinated acrylate polymers, perfluoropolyether polymers, and poly(ethylene glycol)-

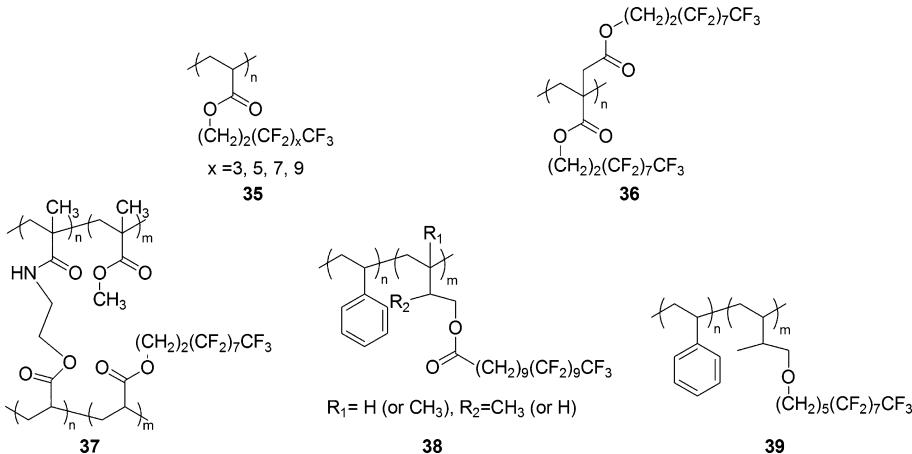
Table 11. Table of Papers Dealing with Fluorinated-Polymer Based FRCs (See Charts 4–8)

coating	coating characteristics	fouling resistance and fouling release performances	ref
poly(perfluoroalkyl (meth)acrylate) 35	$\theta_W = 113\text{--}125^\circ$ $\gamma_S = 5.6\text{--}12.9 \text{ mJ}\cdot\text{m}^{-2}$	control: glass, PTFE ↓ settlement of bacteria <i>Pseudomas</i> and <i>Alteromonas</i> , <i>Ulva</i> spores and barnacles <i>A. amphitrite</i> cyprids	135
poly(perfluorodecanoyl diitaconate) 36	$\theta_{W,adv} = 120.1 \pm 0.3^\circ$ $\theta_{W,rec} = 119.8 \pm 0.4^\circ$ $\gamma_S = 7 \text{ mJ}\cdot\text{m}^{-2}$	—	240
copolymer including heptadecafluorodecylacrylate 37	$\theta_{W,adv} = 111^\circ$ $\theta_{W,rec} = 91^\circ$	better release properties for coatings with the highest cross-link density, the highest receding angle and lowest contact angle hysteresis	130
block copolymer with semifluorinated liquid crystalline side-chains on SEBS 38	$\theta_{W,adv} = 120\text{--}124^\circ$ $\theta_{W,rec} = 82\text{--}87^\circ$ $\Delta\theta \approx 40^\circ$	control: SilasticT2 similar removal of <i>Navicula</i> , ↓ removal of <i>Ulva</i> sporelings	245
PS/PI(25/15)Br-O-H6F8 39	$\theta_W = 90 \pm 4^\circ$	control: glass and SEBS base elastomer ↓ settlement and ↑ removal of <i>Ulva</i> spores	246
random perfluoropolyether graft terpolymer 41a , 41b , 42a , 42b	$\theta_{W,adv} \approx 120^\circ$ $\theta_{W,rec} \approx 96\text{--}100^\circ$ $\Delta\theta \approx 20\text{--}24^\circ$	control: SilasticT2 ↓ settlement, ↑ removal of <i>Ulva</i> spores, ↓ removal of <i>Ulva</i> sporelings	249
PFPE elastomers 43	$\theta_{W,adv} = 114\text{--}127^\circ$ $\theta_{W,rec} = 39\text{--}76^\circ$ $\Delta\theta = 39\text{--}81^\circ$ $\gamma_C = 11.4\text{--}14.8 \text{ mN}\cdot\text{m}^{-1}$ $\gamma_S = 13.4\text{--}16.3 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^P = 0.7\text{--}2.7 \text{ mJ}\cdot\text{m}^{-2}$ $E = 1.5\text{--}90 \text{ MPa}$	control: SilasticT2 ↓ settlement of <i>Ulva</i> spores ↑ removal of <i>Ulva</i> sporelings	250
SABC	$\theta_{W,adv} = 94 \pm 1^\circ$	control: SilasticT2	252, 253
comblike block copolymers with amphiphilic (PEG-fluoro) side chains 46	$\theta_{W,rec} = 34 \pm 1^\circ$ $\Delta\theta = 60 \pm 1^\circ$	similar settlement and ↑ removal of diatom <i>Navicula</i>	
block copolymer with grafted (ethoxylated fluoroalkyl) amphiphilic side chains 47	$\theta_{W,adv} = 107 \pm 2^\circ$ $\theta_{W,rec} = 26 \pm 2^\circ$ $\Delta\theta = 81 \pm 2^\circ$	similar settlement and removal for <i>Ulva</i> sporelings control: SilasticT2 ↓ settlement of <i>Ulva</i> spores ↑ removal of <i>Ulva</i> sporelings and diatom <i>Navicula</i>	257
PS- <i>b</i> -PI block copolymers modified with semifluorinated or PEG or ethoxylated fluoroalkyl side chains	$\theta_{W,adv} = 58\text{--}90^\circ$ (captive bubble)	control: SEBS and glass ↓ settlement of <i>Ulva linza</i> spores ↑ removal of <i>Ulva linza</i> spores	256
PS- <i>b</i> -P(E/B)- <i>b</i> -PI-22F-27P 48	$\theta_{W,adv} = 125 \pm 3^\circ$ $\theta_{W,rec} = 25 \pm 3^\circ$ $\Delta\theta = 100 \pm 3^\circ$	control: SilasticT2 ↓ settlement of <i>Ulva</i> spores ↑ removal of <i>Ulva</i> sporelings and diatom <i>Navicula</i>	258
amphiphilic fluorinated block copolymer S26Sz23_100 49	$\theta_W = 113 \pm 2^\circ$ $\gamma_S = 13.5 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^P = 0.6 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^D = 12.9 \text{ mJ}\cdot\text{m}^{-2}$	control: SEBS and SilasticT2 ↑ removal of <i>Ulva</i> sporelings and ↓ removal of diatom <i>Navicula</i>	259
PFPE-PEG copolymers 51	$\theta_W = 118^\circ$ $\gamma_S = 11.5\text{--}12.7 \text{ mN}\cdot\text{m}^{-1}$	control: PDMS ↓ settlement of diatom <i>Nitzschia</i>	260

Table 11. continued

coating	coating characteristics	fouling resistance and fouling release performances	ref
PFPE/PEG photocurable network	$\theta_W = 108.4\text{--}112.3^\circ$ $\gamma_S = 13.3\text{--}14.4 \text{ mJ}\cdot\text{m}^{-2}$	↓ critical water pressure required to remove 50% of <i>Ulva</i> sporelings but better FR properties for SilasticT2	261
S2, S3			
MRF (PU-fluorinated)	$\theta_W = 109^\circ$	control: glass, PU and SilasticT2	262
MRZ-100 amphiphilic PEG-fluoro	$\theta_W = 88^\circ$	↓ settlement of <i>Ulva</i> spores and ↑ removal of <i>Ulva</i> sporelings	
HBFP-PEG45	$\theta_W = 80.4 \pm 3.3^\circ$	control: glass and SilasticT2	263
	$\gamma_S = 30.07 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^P = 6.60 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^D = 23.47 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S = 31.78 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^{LW} = 27.88 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^+ = 0.64 \text{ mJ}\cdot\text{m}^{-2}$ $\gamma_S^- = 5.89 \text{ mJ}\cdot\text{m}^{-2}$	↓ settlement <i>Ulva</i> spores and ↑ removal of <i>Ulva</i> sporelings	

Chart 4. Perfluoroalkyl Polymers



fluoropolymers, as detailed in the next sections and summarized in Table 11.

4.2.2.2. Perfluoroalkyl Polymers. During the 1990s, studies mainly focused on polymers of fluorinated acrylates (or methacrylates) of the type $\text{CH}_2=\text{CH}-\text{COOR}_f$ (Chart 4), where R_f is a bulky fluoroalkyl group (e.g., $-\text{CF}(\text{CF}_3)_2$), which are amorphous and have better solvent solubility than PTFE. Tsibouklis and co-workers^{135,240,241} developed poly(perfluoro(meth)acrylate) polymers 35 to design smooth film structures which inhibit marine organism settlement. They showed that the perfluorocarbon side-chains segregated preferentially toward the surface,²⁴² and the film presented a surface energy lower than $10 \text{ mJ}\cdot\text{m}^{-2}$. These fluorinated films showed low settlement of bacteria *Pseudomonas*, alga *Ulva*, and barnacle *A. amphitrite*.²⁴¹ Analogous materials containing two pendant fluorocarbon chains poly($1H,1H,2H,2H$ -perfluorodecanoyl diitaconate) 36 exhibited a limited resistance to colonization by marine organisms although low surface energy values close to $7\text{--}8 \text{ mJ}\cdot\text{m}^{-2}$ were reported by Pullin et al.²⁴⁰ The poor AF

performance of films immersed in seawater over prolonged periods of time was assigned to the increase of the base component of the surface energy γ_S^- with immersion time.

To overcome the issue of surface reconstruction of perfluoroalkyl-based coatings with immersion time, fluorinated coatings were prepared by cross-linking a copolymer of $1H,1H,2H,2H$ -heptadecafluorodecyl acrylate and acrylic acid with a copolymer of poly(2-isopropenyl-2-oxazoline) and methyl methacrylate 37 at different molar ratios.¹³⁰ The latter exhibited low water CA hysteresis and therefore the best release properties. The fluorinated moieties were found to self-assemble at the air–liquid interface from a water media to produce an array of closely packed, oriented CF_3 -terminated perfluoroalkyl groups on the surface. Because of a high cross-link density, the oriented perfluoroalkyl groups were strictly immobilized and tended to resist both infiltration of bioadhesive molecules and adhesive-induced molecular rearrangement. By virtue of the low energy of the surface ($12\text{--}17 \text{ mJ}\cdot\text{m}^{-2}$), its interface with the bioadhesive was not strong, and

due to the high resistance of the surface to molecular diffusion and rearrangement, its interface to the marine bioadhesive was sharp, well-defined, and easily cleaved.²⁴³ The resistance to marine biofouling appeared to be also related to low CA hysteresis, which is due to the immobilized, closely packed, oriented CF₃-terminated perfluoroalkyl groups.¹³⁰ Moreover, the authors showed that the adhesive release properties of the coating did not correlate well with the surface energy of the coating or its static water CA but correlate directly with the water receding angle and CA hysteresis. Fluorinated-(meth)acrylate block polymers containing semifluorinated liquid crystalline side-chains **38** were preferred over perfluorinated ones (**35**, **36**, **37**) because alkyl spacers in the partially fluorinated side-chains lead to a better orientation of the perfluoro groups and to a well-packed fluorinated surface (Figure 24).^{244,245} These FRCs were shown to combine the

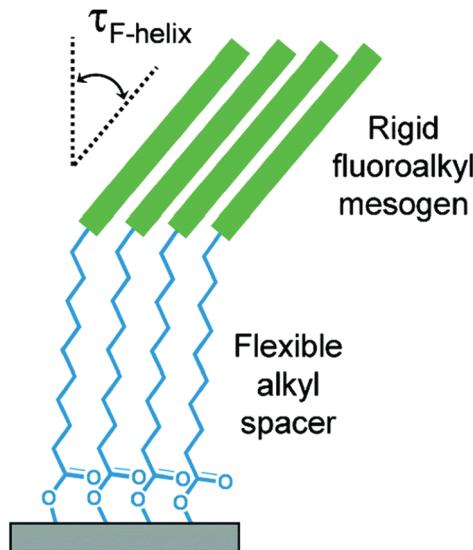


Figure 24. Liquid crystalline self-assembly of the semifluorinated side chains to form a nonreconstructing hydrophobic surface under water. Reprinted with permission from ref 245. Copyright 2006 American Chemical Society.

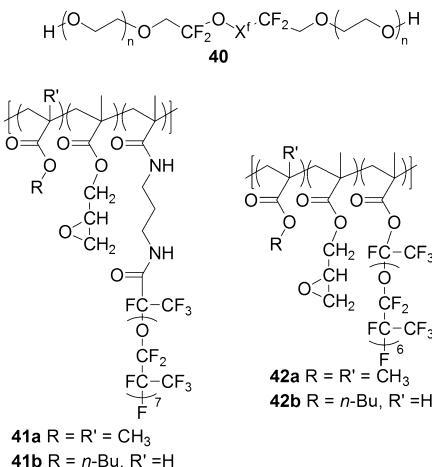
advantages of the amorphous nature of the long hydrocarbon part, imparting processing solvent solubility, and the liquid crystalline nature of the fluorocarbon part, imparting surface stability, without the need for chemical cross-linking.

Indeed, in the absence of a crystalline phase these polymers are expected to reconstruct after immersion in water, exposing the more polar ester groups at the polymer–water interface. In addition, the perfluoro group was shown to overcome the polarity of the carbonyl group, resulting in an advancing water CA of 120° and a critical surface tension of *ca.* 14 mN·m⁻¹, even lower than the PTFE one (*ca.* 18 mN·m⁻¹). These fluorinated block copolymers were applied as a top-coat onto polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS) used as a bottom primer layer. The polystyrene (PS) block was shown to improve the polymer compatibility at the interface with the underlayer by anchoring the PS block of the fluorinated copolymer in the cylindrical PS domains of SEBS. The coating was found to be effective in preventing settlement and release of sporelings of the alga *Ulva linza*. The FR ability was comparable to that of Silastic T2 PDMS elastomer. However, the copolymer was not effective in the release of cells of *N. perminuta* diatoms.

Effective removal of alga *Ulva* was also achieved with similar coatings based on poly(styrene)-*block*-poly(isoprene) block copolymers (PS-PI) modified with semifluorinated ether-linked moieties **39** applied on a SEBS undercoat. Therefore, coatings having the best release properties had both the highest resistance to surface rearrangement and the lowest CA hysteresis.²⁴⁶

4.2.2.3. Perfluoropolyether Polymers. In 2003, Brady^{247,248} first patented the use of fluorinated polyurethane elastomers as FRCs. A poly(perfluoro(oxymethylene-*r*-oxyethylene)dimethylol)-terminated oligomer **40** (also referred to as a perfluoropolyether or PFPE diol) was added to react with a diisocyanate component in the presence of a cross-linker and dibutyltin dilaurate **16** as catalyst. The proportion of the starting materials was chosen to control the cross-link density of the polymer, which in turn controls both its degree of elasticity and its resistance to physical damages. Fluorine content ranging from 9 to 10 mol % led to a surface energy ranging from 27 to 25 mJ·m⁻² and an elastic modulus *E* ranging from 3 to 7 MPa, respectively. DeSimone and co-workers have intensively investigated the FR properties of perfluoropolyether polymers. Cross-linkable random PFPE graft terpolymers containing various alkyl (meth)acrylate monomers with glycidyl methacrylate as the curable monomer (**41a**, **41b**, **42a**, **42b**; Chart 5) were developed.²⁴⁹ PFPE macromonomers were

Chart 5. Perfluoropolyether Polymers



investigated to provide a low surface energy by surface enrichment. Through variation of composition and curing conditions, the authors found that the cross-link density significantly affected the CA hysteresis, increasing the receding water CA value, while advancing CA values remained constant. The PFPE surface enrichment was also shown to depend on the glass transition temperature (*T_g*) values of the polymer chains between cross-linking points. It appeared that the higher *T_g* values enhanced the receding CA and restricted chain mobility. These coatings were shown to prevent the accumulation of alga *Ulva* in comparison to PDMS and glass standards, and they have characteristics which facilitate its release under suitable hydrodynamic conditions.

More recently, difunctional PFPE macromonomers with methacrylate and styrene moieties as end groups (**43**)²⁵⁰ and blends of distyrenyl-modified PFPE (sPFPE, **44**) with a fluorinated derivative of a styrenesulfonic ester monomer (SS, **45**)²⁵¹ (Chart 6) were chosen to form cross-linkable

Chart 6. Perfluoropolyether Polymers

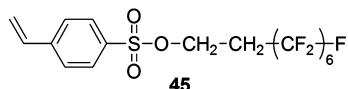
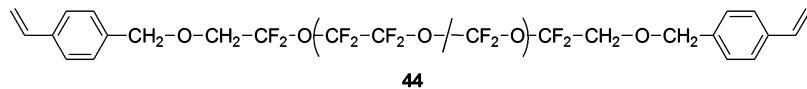
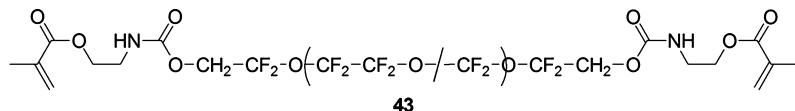
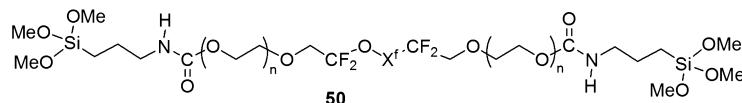
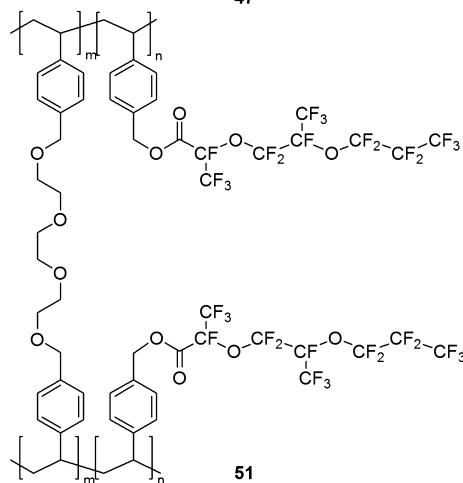
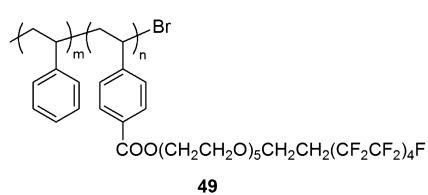
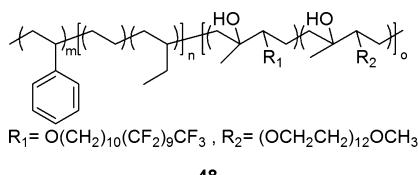
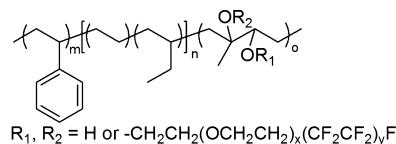
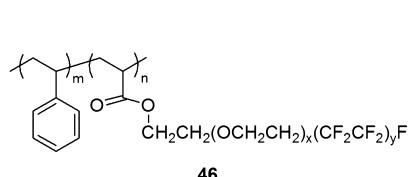


Chart 7. Poly(ethylene glycol)-fluoropolymers



fluoropolymers *via* a photochemical (UV curing) process. These latter copolymer networks (sPFPE-SS) exhibited elastic modulus values from 1.5 to 90 MPa with a critical surface tension of 8.6–16 mN·m⁻¹, by varying the cross-link density, i.e. the molecular weight of the α,ω -distyrenyl-modified PFPE (44). All of the PFPE surfaces were highly hydrophobic with a water advancing CA greater than 110° and a receding CA from 76° to 39°. Upon contact with water, the rotation and relaxation of the polar hydrophilic functionalities, such as the urethane segments in the end groups of the PFPE chains or the -CF₂CH₂O- units, led to a high CA hysteresis. Settlement and release assays involving zoospores of alga *Ulva linza* demonstrated that the coatings with low surface energy, elastic modulus, and CA hysteresis prevented the accumulation of fouling in comparison to the case of a PDMS elastomer standard and had characteristics which facilitated their release under suitable hydrodynamic conditions.

4.2.2.4. Poly(ethylene glycol)-fluoropolymers. Although fluoropolymer-based FRCs were shown to be efficient in preventing and releasing fouling organisms such as alga *Ulva*, they may be less efficient concerning the adhesion of diatoms.²⁴⁵ Since one of the challenges in the area of FR marine coatings technology is to develop a coating that resists strong adhesion of all types of marine fouling, more polar surfaces, i.e. coatings incorporating poly(ethylene glycol) (PEG) moieties combined with fluorinated moieties, have been investigated. PEG surfaces are known for their resistance to protein adsorption and cell adhesion, and they have also demonstrated resistance to settlement and release of marine fouling organisms. Despite a relatively high surface energy (>43 mJ·m⁻²), PEG-coated surfaces have a low interfacial energy with water, and their resistance to adhesion was reported to rely on a steric repulsion of the adhesive molecule caused by the hydrated PEG.²⁴⁵ Amphiphilic block copolymers based on

polystyrene (PS) and polyacrylate (PA) blocks where the polyacrylate block acts as an anchor for the amphiphilic ethoxylated perfluoroalkyl side chains **46** (Chart 7) were used as FRCs.^{252,253} When assembled on a substrate, the PS block played the role of a substrate binder while the other block exposed the amphiphilic side chains to the air–polymer interface. These comblike block copolymers containing PEG-fluoro side-chains linked by an ester group were tested against the green alga *Ulva* and cells of a diatom *Navicula*.²⁵² The settlement of diatoms was comparable to that of a PDMS elastomer, but the strength of adhesion was much lower than that of PDMS, with $81 \pm 5\%$ of removal for the amphiphilic surface in contrast to $11 \pm 4\%$ for the PDMS surface. The high removal of diatoms from the amphiphilic surface was explained by the molecular reconstruction of the surface, which became as hydrophilic as a PEGylated surface when immersed into water (Figure 25), and by the fact that diatoms adhered weakly to hydrophilic surfaces.

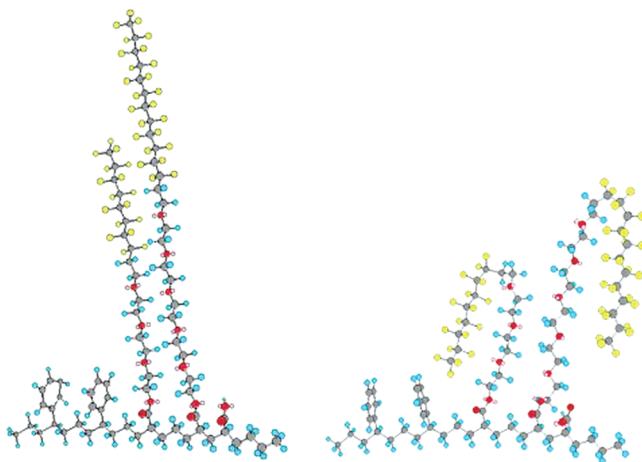


Figure 25. Proposed mechanism for surface reconstruction of the ethoxylated-fluoroalkyl side-chains upon immersion of the surface in water. The picture on the left indicates the orientation of side chains in air whereas that on the right shows the effect of water immersion. Reprinted with permission from ref 252. Copyright 2006 American Chemical Society.

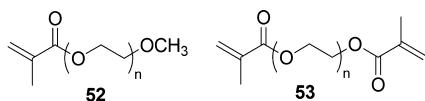
In the case of *Ulva* zoospores, both the settlement inhibition and the removal of fouling were comparable to those for PDMS; the strength of adhesion was lower than that of glass. Other types of amphiphilic block copolymers were reported in the patent literature, where the side-chains were linked on such vinyl polymers *via* ester²⁵⁴ or amide²⁵⁵ groups.

Analogous studies were performed using diblock or triblock copolymers containing PS and polyisoprene (PI) blocks, where the vinyl groups within the polymer backbone or on pendant side-chains can be converted to hydroxyl or halo groups. These latter groups were further used to create ether linkages to side-chains including semifluorinated alcohols, PEG derivatives, or ethoxylated fluoroalkyl alcohols **47**.²⁵⁶ The ether linkage was reported to be more resistant to the marine environment as opposed to ester linkages, which can undergo hydrolysis over time. The authors mentioned that the length of PS blocks dictated the solubility of the corresponding semifluorinated polymers. These copolymers exhibited elastomeric properties and strong adhesion to substrates. As FR properties rely on the elastic modulus of the surface, these surface-active block copolymer (SABC) were also blended with a thermoplastic

elastomer such as a commercially available Kraton styrene–ethylene–butylene–styrene (SEBS) triblock copolymer or deposited on this elastomeric base. Amphiphilic block copolymers produced from the modification of triblock copolymers of polystyrene-block-poly(ethylene-*ran*-butylene)-block-polysisoprene (PS-*b*-P(E/B)-*b*-PI) with ethoxylated fluoroalkyl side chains were also studied by Weinman et al.²⁵⁷ A high CA hysteresis was observed, suggesting a dynamic surface capable of facile reordering of the side chains to readily orient the hydrophilic PEGylated groups at the surface, which is similar to the mechanism proposed by Krishnan et al.²⁵² These amphiphilic copolymers are capable of both resisting settlement and enhancing the release of zoospores as well as improving the release of sporelings of the green alga *Ulva* and the diatom *Navicula*, and therefore, antifouling and FR properties were better than those of PDMS elastomers. In addition, reducing the elastic modulus of the thermoplastic elastomer base layer used in the coating from 18 to 1.2 MPa enhanced the release of sporelings of *Ulva*.²⁵⁷ Similarly, Park et al.²⁵⁸ prepared modified triblock PS-*b*-P(E/B)-*b*-PI copolymers with both discrete PEG and semifluorinated side chains instead of only one type of PEG-fluorinated side chains (**48**). This enabled tuning of the proportion between PEG and fluorinated components. The authors demonstrated a lower settlement of *Ulva* zoospores and *Navicula* diatoms for the coating incorporating of a large molar proportion of PEG (from 19% fluoro/28% PEG to 0% fluoro/33% PEG). A positive correlation between levels of removal of attached spores and low surface wettability was demonstrated, which is consistent with previous results on self-assembled monolayers.²⁵ In addition, bilayer coatings using a SEBS substrate and an upper SABC layer showed a pseudobarnacle pull-off force three times lower than that required for uncoated SEBS substrates, demonstrating their ability to enhance fouling removal. Functionalized amphiphilic PEG-fluorinated polystyrene block copolymer **49** containing PS blocks and amphiphilic PS carrying PEG-PTFE side chains also exhibited antifouling and FR properties for alga *Ulva linza* and diatom *N. perminuta*.²⁵⁹ In addition, these films were nanostructured with well-defined morphological features, including spherical and lying cylindrical nanodomains of the PS discrete phase segregated from the amphiphilic continuous matrix (PS carrying PEG-PTFE).

In most of the studies dealing with PEG-fluorinated FRCs, long perfluoroalkyl chains (C_nF_{2n+1} , with $n \geq 8$) are generally used to achieve a significant low surface energy and hydrophobicity. However, their degradation gives environmentally persistent perfluorooctanoic acid, which can resist degradation and bioaccumulation in human and animal tissue and possesses a long biological half-life. To overcome this issue, amphiphilic coatings based on PEG and PFPE chains **51** were developed, as PFPE polymers are biodegradable and exhibit a low surface energy ($<13 \text{ mJ}\cdot\text{m}^{-2}$) and reduced settlement of diatoms compared with a PDMS standard.²⁶⁰ More recently, DeSimone and co-workers²⁶¹ pursued their studies on photocurable PFPE with the synthesis of amphiphilic PFPE/PEG networks as FRCs. Both mono- and dimethacryloxy-functionalized PEG macromonomers (PEG-MA (**52**) and PEG-DMA (**53**), respectively) (Chart 8) were cross-linked with reactive dimethacryloxy-functionalized PFPE oligomers such as PFPE-DMA (**43**) to lead to networks with flexible and more restricted PEG chains, respectively. Since the relative content of PEG was kept low in the networks, all the cured films exhibited low surface energies ranging from 13.3 to

Chart 8. Mono- and Dimethacryloxy-Functionalized PEG Macromonomers



14.4 $\text{mJ}\cdot\text{m}^{-2}$. The functional PEG macromonomers were shown to decrease the elastic modulus of films from 13.2 MPa for pure PFPE-DMA to 11.8 MPa for 10 wt % of PEG-DMA and to 6.1 MPa for 10 wt % of PEG-MA within the networks. The PFPE/10%-PEG-MA coating displayed better FR performance against *Ulva* sporelings and removal of juvenile barnacles in comparison to all the PFPE/PEG-DMA coatings, which was attributed to the flexibility of PEG-MA chains allowing the PEG to migrate to the surface of the PFPE/PEG-MA blend. Nevertheless, the best PFPE/PEG coating was not as efficient as a PDMS elastomer standard. More complex polymer architectures were explored with tethered dendritic polyol modified by PEGylated, fluorinated, or PEG-fluorinated moieties, which exhibited similar or better *Ulva* sporelings removal than from a FR PDMS standard.²⁶² Surface-tethered hyperbranched polymers containing both fluorinated and PEGylated groups (HBFP-PEG) were reported as low protein adsorption and high FR coatings at an optimal composition of hydrophobic and hydrophilic monomers of 45 wt % for the PEG component (Figure 26).²⁶³ Compositional and topographical structures were observed due to the occurrence of phase segregation of the fluoropolymer and PEG domains, resulting in a higher release of green alga *Ulva linza* compared to PDMS.^{264,265} Similarly, the HBFP-PEG network surfaces exhibited surface reconstruction when placed in polar media, such as water, which resulted in surface segregation of the more hydrophilic PEG component to the coating/liquid interface.²⁶³

Good AF performances were also reported for condensation-cured PEG-perfluorinated coatings synthesized from α,ω -trimethoxyalkylsilyl PFPE cross-linked with alkyltrialkoxysilanes 50.²⁶⁶ All of these fluorinated resins or elastomers combining for some PEG side chains exhibited promising antifouling and FR performances. As yet, none of them have been introduced on the marine coating market. The only fluorinated-based systems commercially available are polysiloxane-based elastomers comprising fluorinated oils (see section 5.3).

4.2.3. Commercially Available Fouling Release Coatings. The current commercially available FRCs are reported in Table 12 as well as information about their formulation and their specifications. This list could be not exhaustive and has been established with technical and safety data sheets available on the marine paint companies' Web sites. Most of these coatings are based on condensation-cured silicone elastomers. The incorporation of additive oils is generally not explicitly mentioned by manufacturers. Nevertheless, in three-part systems, the silicone precursor, cross-linker, and catalyst are separated in three different cans, whereas, in two-part systems, silicone precursor and cross-linker are conditioned in one can and catalyst in another can.

4.3. Drawbacks of Fouling Release Coatings

PDMS-derived coatings are particularly susceptible to fouling on idle periods, and concerns also exist about their stability in water, their long-term durability, and their impact on the surrounding environment. While most macrofouling organisms cannot easily adhere to FRCs when the coated surface is submitted to mechanical stresses, these coatings do not prevent the buildup of slime layers which are mainly composed of diatoms and bacteria.^{26,41,42,267} Diatoms are well-known to adhere more strongly to hydrophobic surfaces, and to resist removal even at high hydrodynamic stress, withstanding water speeds of up to 30 knots.⁴¹ While slime layers may also develop on biocidal AF coatings,^{24,26} diatom slimes are a substantial

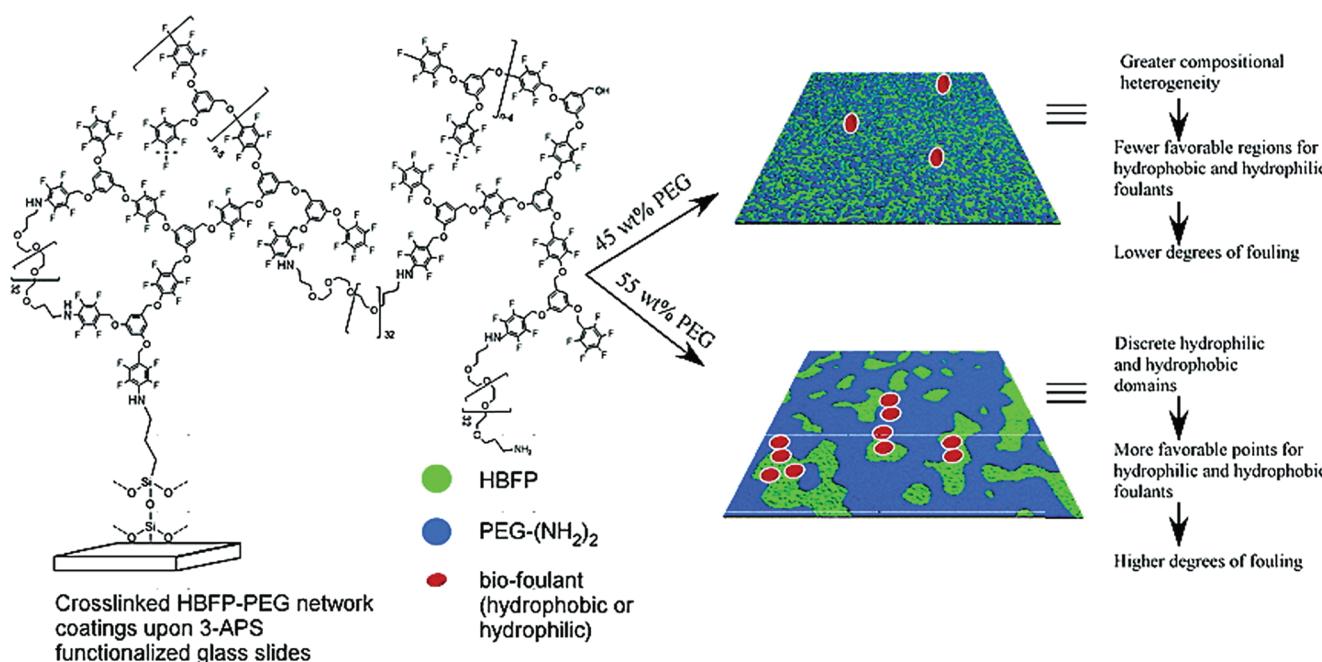


Figure 26. (Left) Schematic illustrating the structure of polymer networks comprising hyperbranched fluoropolymers (HBFP) and poly(ethylene glycol) chains (PEG). (Right) The HBFP-PEG network that contains 45% of PEG exhibits the highest resistance toward protein adsorption. Reprinted with permission from ref 263. Copyright 2005 American Chemical Society.

Table 12. Commercially Available Fouling Release Coatings

product type	producer	top-coat	tie-coat	formulation			specifications
				cure system	catalyst	cross-linker	
silicone	Chugoku Marine Paints	Bioclean HB	Bioclean Tie Coat	not known			
	Fujifilm	Surface Coat	Tie-Coat	two-part condensation	16	15	speed >10 knots, 6–10% fuel savings
	Hempel	Hempasil 77100	Hempasil Nexus	two-part condensation	16	13, 15	activity >50%, speed >25 knots
		Hempasil 77500	Hempasil Nexus	two-part condensation	16	13, 15	activity >75%, speed >15 knots
	International Paint	Intersleek 425	Intersleek 386	three-part condensation	17	13	speed >30 knots
		Intersleek700	Intersleek 737	three-part condensation	17	13	high activity vessels, speed >15 knots
	Jotun	SeaLion	SeaLion Tie-Coat	three-part condensation	19	13, 15	high activity, high speed, 1.5% fuel savings
	Korean Chemical Company	Lo-Frick A/F100	Lo-Frick T200	two-part condensation			high speed
	Neosil BV	Neosil	Neosil midcoat	two-part condensation	13		6% fuel savings
	Nippon Paint Marine Coatings	Ecolosilk	Ecolosilk Tie-Coat	not known			speed >15 knots
PPG	PPG	ABC Release	ABC Release 670	two-part			
		SigmaGlide 890	SigmaGlide 790	two-part condensation	18	13	
		SigmaGlide 990	SigmaGlide 790	two-part condensation	18	13	5% fuel savings
	Sherwin Williams	SeaGuard Surface Coat	SeaGuard Tie-coat	two-part	16	13	speed >10 knots, 6–10% fuel savings
	Transocean	Ultima System	Ultima Tie-Coat	two-part			high speed
fluoro-silicone	International Paint	Intersleek 900	Intersleek 737	three-part condensation	17	13	all vessel types, speed >10 knots, 9% fuel savings 50% reduction in slime compared to Intersleek700
hydrogel silicone	Hempel	Hempasil X3 87500	Hempasil Nexus	two-part condensation	16	13, 15	activity >50% speed >8 knots 8% fuel savings
surface “engineered with nanoscale springs”	Jotun	SeaLion Repulse	SeaLion Tie-Coat	three-part condensation	19	13, 15	high activity high speed
nanotubes incorporated	Nanocyl	Biocyl		two-part condensation or hydrosilylation			speed >4 knots

drawback for FRCs, as biofilm contributes to increase frictional resistance of ships^{49,186} and consequently to reduce the efficiency of FRCs upon drag reduction and fuel saving. Slime layers may also influence the subsequent settlement of larvae of macrofouling organisms.¹³ Another drawback of FRCs is related to their stability in water. A silicone RTV11 coating exhibited a mass loss of 0.02 wt %/week when immersed in water. This mass loss was attributed to the removal of low molar mass materials including cyclic and linear species, depolymerization, and loss of CaCO₃.²⁰⁴ This coating was also subject to significant alterations in their morphology and mechanical properties due to the formation of Ca-rich surface-associated aggregates resulting from complexation reactions involving calcium present in seawater.²⁰⁶ Moreover, several studies have pointed out the decreasing of water CA of silicone^{204,268,269} and some fluoropolymer-based coatings^{130,240,268} when immersed in water. This phenomenon was attributed to the thermodynamically driven rearrangement of polymer chains close to the surface with polar functionality brought to the polymer–water interface. The increased polarity

of FRCs might enable interactions with secreted bioadhesives and result in stronger attachment of biofouling and loss of FR properties. Nevertheless, the incorporation of relatively incompatible low-viscosity silicone oil in the formulation has been shown to delay the substantial changes in surface chemistry upon water immersion.^{155,269} As previously mentioned (see section 4.2.1.4), FRCs suffer from poor adhesion to ship hulls, and a tie-coat is required to provide good adhesion between the top-coat and the epoxy-based anticorrosive underlayer. Moreover, due to their low elastic modulus, the soft silicone-based FRCs exhibit poor mechanical strength and are subjected to problems of cutting, tearing, and puncturing. Mechanical damage can frequently happen on the sides of ships caused by anchor chains and fender and mooring impact. Underwater cleaning needs to be carried out with soft brushes, which may not remove all organisms that have settled. In addition, mechanical damage will result in local unprotected areas where barnacles can achieve a solid attachment.²³⁸ These mechanical defects eventually require specific touch-ups in dry-dock. Finally, some concerns now emerge from the use of

Table 13. Table of Papers Dealing with Hybrid Silicone FRCs

coating	coating characteristics	fouling resistance and fouling release performances	ref
Sylgard184 + 0.05–0.2 wt % carbon nanotubes	$\theta_W = 104^\circ \pm 2^\circ$ $\theta_{W,adv} = 116^\circ \pm 3^\circ$ $\theta_{W,rec} = 85^\circ \pm 2^\circ$ $\Delta\theta = 31^\circ$ $\gamma_S \approx 25 \text{ mJ}\cdot\text{m}^{-2}$	control: Sylgard184 ↓ <i>A. amphitrite</i> barnacle adhesion strengths and ↑ removal of <i>Ulva</i> spores	174, 277
cross-linked polysiloxane–polyurethane coating with microtopographical domains	$\theta_W \approx 100^\circ$ $\theta_{W,adv} = 102.9\text{--}105.6^\circ$ $\theta_{W,rec} = 84.3\text{--}92.8^\circ$ $\Delta\theta = 10.7\text{--}21.3^\circ$ $\gamma_S = 11.05\text{--}16.69 \text{ mJ}\cdot\text{m}^{-2}$	↓ adhesion strength of <i>A. amphitrite</i> barnacles for the PDMS-PU coatings with microtopographical domains and the lowest $\Delta\theta$	281
polysiloxane–polyurethane from library of hydroxyalkyl carbamate and dihydroxyalkyl carbamate-terminated PDMS cross-linked with poly(<i>e</i> -caprolactone)	$\theta_W = 106\text{--}118^\circ$ $\theta_{W,adv} = 109\text{--}122^\circ$ $\theta_{W,rec} = 89\text{--}101^\circ$ $\Delta\theta = 15\text{--}22^\circ$ $E = 1100 \text{ MPa}$ $\theta_W = 95\text{--}100^\circ$	control: silicone ↓ coverage, ↑ removal of bacteria <i>C. lytica</i> ↓ removal of <i>H. pacifica</i> ↓ removal of <i>Ulva</i> sporelings at low pressure ↓ adhesion strength of <i>A. amphitrite</i> barnacles	282
polysiloxane–polyurethane from monoaminopropyl-terminated PDMS cross-linked with a library of acrylic polyols composed of HEA, BA, BMA	$\theta_W > 100^\circ$ $\gamma_S = 22\text{--}28 \text{ mJ}\cdot\text{m}^{-1}$	↑ removal of <i>Ulva</i> sporelings and <i>Navicula</i> biofilm for coatings with higher content of HEA and BA in the acrylic polyol	283
polysiloxane–polyurethane from monoaminopropyl-terminated PDMS cross-linked with a polycaprolactone polyol	$\theta_W = 95\text{--}100^\circ$ $\gamma_S = 22\text{--}28 \text{ mJ}\cdot\text{m}^{-1}$	control: PU, silicone (SilasticT2, DC3140) ↓ <i>C. lytica</i> biofilm retention similar pull-off adhesion of pseudobarnacles ↓ <i>N. incerta</i> settlement and ↑ removal for coatings with short PDMS chains similar <i>Ulva</i> removal for coating with long PDMS chains, ↓ removal for coatings with short PDMS chains ↑ or similar removal of live barnacles	202
A12 M (PDMS-polyurea copolymer) 54			
A12MF (fluorinated) 55			
A12M/POSS 56		control: glass and PDMS SilasticT2	291
A12M/clay		↑ coverage and ↑ removal of <i>Ulva</i> sporelings	
silicone (15–30%) modified epoxy resin 57	$\theta_{W,adv} = 110\text{--}140^\circ$ $\theta_{W,rec} = 30\text{--}70^\circ$ $\Delta\theta = 50\text{--}110^\circ$ $E > 86 \text{ MPa}$ $\gamma_S = 23.7\text{--}28.2 \pm 0.3 \text{ mJ}\cdot\text{m}^{-2}$ $E = 3.2\text{--}4.1 \pm 0.2 \text{ MPa}$	control: unmodified epoxy-resin ↓ pseudobarnacle adhesion strength slower rate for fouling coverage better fouling release	293
oxetane (10–20%)-toughened, UV curable, epoxy-siloxane 58 and 59	$\gamma_S = 13\text{--}14 \text{ mJ}\cdot\text{m}^{-2}$ $\theta_W \approx 109^\circ$ $\Delta\theta \approx 15^\circ$ $E = 11\text{--}18 \text{ MPa}$	control: Silastic3140 similar <i>C. lytica</i> and <i>H. pacifica</i> bacterial biofilm removal ↓ (similar) diatom <i>N. incerta</i> removal for 10% (20%) oxetane coating similar pseudobarnacle shear release stress ↑ <i>Ulva</i> sporelings release than SilasticT2	294
Films of epoxy-terminated star oligofluorosiloxanes cross-linked with diamino-PDMS (IVa) 60	$\theta_W = 109^\circ$ $\theta_{W,adv} = 114^\circ$ $\theta_{W,rec} = 84^\circ$ $\Delta\theta = 23^\circ$	control: Veridian (FRC) similar removal of <i>Ulva linza</i> ↑ <i>Ulva linza</i> removal compared with equivalent star oligosiloxanes	295
silicone FRC cross-linked with a fluoro-silicone polymer 61		control: silicone FRC without fluorinated polymer ↓ pseudobarnacles adhesion strength	296
PDMS elastomer cross-linked with (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane 62	$\theta_{W,adv} = 118.8\text{--}135.9^\circ$	—	297
blends of PDMS + fluorinated/siloxane copolymer 65	$\theta_{W,rec} = 54.6\text{--}101.6^\circ$ $\theta_W = 119\text{--}122^\circ$ $\gamma_S = 12.2 \text{ mJ}\cdot\text{m}^{-1}$	control: Pure PDMS ↓ settlement of <i>A. amphitrite</i> barnacles cyprids ↓ adhesion strength of barnacles and <i>Ulva</i>	299
blends of PDMS + PEGylated-fluorinated/siloxane copolymer 66	$\theta_W = 112\text{--}125^\circ$	control: pure PDMS	301

Table 13. continued

coating	coating characteristics	fouling resistance and fouling release performances	ref
Hempasil X3	$\theta_{CH2I2} = 79\text{--}96^\circ$ $\gamma_s = 11.0\text{--}19.8 \text{ mJ}\cdot\text{m}^{-2}$	↑ <i>Ulva</i> removal	
Hydrogel-modified silicone FRC	$\theta_w = 96^\circ \pm 1^\circ$ $\theta_{w,adv} = 96^\circ \pm 1^\circ$ $\theta_{w,rec} = 23^\circ \pm 1^\circ$ $\Delta\theta = 73^\circ$	control: pure PDMS FRC and fluoropolymer-silicone FRC ↓ settlement of bacteria <i>C. lytica</i> and diatom <i>N. incerta</i>	302
PDMS (hydrosilylation or epoxy-cure) + attached triclosan 67 and 68	$\theta_w = 91\text{--}108^\circ$ $\gamma_s = 20\text{--}30 \text{ mJ}\cdot\text{m}^{-1}$ $E = 0.07\text{--}68 \text{ MPa}$ $T_g = 50\text{--}56^\circ\text{C}$ $\theta_w = 106\text{--}114^\circ$ $E = 0.3\text{--}1.6 \text{ MPa}$	↑ removal of <i>C. lytica</i> ↓ settlement of <i>A. amphitrite</i> barnacles and ↓ adhesion strength ↓ barnacle settlement for coatings with modulus in the range of 0.1–10 MPa	313
vinylic- (and methacryloxypropyl) terminated PDMS cured by hydrosilylation with tethered (meth)acrylate Tricosan	—	control: Intersleek425	310
condensation-cured polysiloxane containing 29 wt % QAS moieties 69	— — — — —	29 day immersion: ↓ barnacle settlement (similar to Cu ablative paint) 85 day immersion: similar barnacle settlement (higher than for Cu ablative paint) control: silicone	314
PU coating containing an amphiphilic zwitterionic pentablock PSBMA-PEG-PDMS-PEG-PSBMA 71	— — — — —	>80% reduction in bacteria <i>C. lytica</i> biofilm retention >90% reduction in biofilm growth of diatom <i>Navicula incerta</i> control: Intersleek700 and 900, SilasticT2, DC3140 silicone similar biofilm coverage and ↓ adhesion strength for <i>C. lytica</i> , <i>H. pacifica</i> ↓ settlement and ↑ removal for <i>N. incerta</i> (similar to pure PU) ↓ adhesion strength of pseudobarnacles	323

FRCs and their environmental impacts, particularly for FRCs exhibiting silicone oils at the coating surface. Indeed, when added to water, silicone oils adsorb to biological and mineral suspended solids and are deposited with them to the sediments.²⁷⁰ At high concentrations, sedimented PDMS may build up oil films on sediments and alter their permeability.²⁷¹ The PDMS used in FRCs has low vapor pressure and negligible water solubility; hence, the coatings neither dissolve in the water phase nor evaporate to the atmosphere. Consequently, they are extremely persistent but they are neither significantly bioaccumulated nor is their soluble fraction very toxic.²⁷¹ The potential physicomechanical effects of leaching oils on aquatic and benthic organisms such as trapping and suffocating of organisms have also been pointed out.²⁷¹ However, Truby et al.¹⁵⁵ demonstrated that the nonbonded oil lost from a silicone coating over one year of laboratory exposure in salt water was less than 1.1 wt %, and with a minimal toxicity to shrimp and fish. In addition to silicone oils, it has been shown that non-cross-linked PDMS^{20,272} and catalysts²⁷³ can migrate to the surface of silicone FRCs. Berglin and Gatenhom²⁰ suggested that uncross-linked PDMS can be incorporated into the adhesive plaque of barnacles grown on silicone coatings. Recently, Rittschof et al.²⁷⁴ demonstrated that components at the surface of silicone FRCs may alter enzyme activity in curing barnacle glue. This alteration of enzyme activity may play a role in the frequent production of atypical soft, thick glue by barnacles growing on silicone polymers.^{20,148,175} However, despite these assumptions on effects of leaching oils or uncross-

linked chains, it is noteworthy that biocidal AF coatings have a significantly worse impact on marine environments than FRCs.

5. HYBRID SILICONE-BASED FOULING RELEASE COATINGS

To improve the adhesion and the durability of silicone-based coating materials while retaining the inherent FR properties of the silicone component, numerous synthetic pathways have been attempted in the literature including the incorporation of nanofillers, the modification of the silicone matrix with polyurethane, epoxy, or fluorinated segments, or the introduction of antifoulants (Table 13).

5.1. Silicone Incorporating Nanofillers

Natural sepiolite nanofibers ($(\text{Mg}_4\text{Si}_6\text{O}_{15})(\text{OH})_2\cdot6\text{H}_2\text{O}$) were incorporated into the hydrosilylation-cured silicone coating called Sylgard 184 to enhance its mechanical properties without weakening its antifouling and FR properties.²⁷⁵ From about 0.1 to 5 μm in length and from 5 to 40 nm in diameter, these nanofillers contributed to the progressive increase in the tensile modulus of the coating with increased loading (from 2.6 MPa for the unloaded formulation to 6 MPa at 10 wt % loading). The release of *Ulva* zoospores and sporelings was improved, but the adhesion strength of *A. amphitrite* larvae was higher than that on the unfilled PDMS. In contrast to sepiolite, the bulk properties (i.e., tensile modulus) of PDMS were not affected by the incorporation of low amounts of multiwall carbon nanotubes (MWCNTs) (up to 0.2 wt %)²⁷⁵ as well as the surface properties before water immersion ($\theta_w = 104^\circ$ for

both pure and filled-PDMS).²⁰¹ The incorporation of MWCNTs was shown to reduce the loss of hydrophobicity of PDMS coatings upon water immersion, with θ_w values of 92° and 97° for the pure PDMS and the 0.1 wt % MWCNTs-filled PDMS after 120 h of immersion, respectively.²⁰¹ The authors hypothesized that, due to the extremely favorable CH- π electronic interactions involving methyl groups of the PDMS and aromatic rings of the MWCNTs, the PDMS chains become less mobile and the top surface reorganization is no longer observed or at least it is strongly reduced when carbon nanotubes are dispersed in silicone-based coatings.²⁷⁶ The addition of small amounts of MWCNTs improved the release of *Ulva* zoospores and sporelings. Moreover, the addition of only 0.05 wt % of MWCNTs to unfilled PDMS more than halved the critical removal stress of adult *A. amphitrite* barnacles.¹⁷⁴ These results were shown to be affected by the nanotubes dispersion within the silicone matrix, as they could easily agglomerate in bundles due to strong interparticle π - π electronic interactions.^{275,277} The authors showed that preparing a 0.1 wt % MWCNTs–silicone coating by dilution of a premix Biocyl containing 2.5 wt % MWCNTs predispersed and disaggregated in a PDMS resin yielded coatings with *ca.* 40% improved FR properties over those where MWCNTs were dispersed directly in the polymer matrix.

5.2. Silicone Modification with Polyurethane or Epoxy Segments

PDMS-modified polyurethane (PU) and epoxy resins have been explored to improve the adhesion and durability of FRCs. One of the first patents for AF coatings based on both silicone and PU technologies was filed in 1991 by Brooks.²⁷⁸ This patent dealt with the preparation of an interpenetrating polymer network made from co-curing a siloxane elastomer and a PU. Cross-linked silicone elastomer networks containing domains of PU, poly(urea), or poly(urethane-urea) with interpenetration of the two polymer networks at the boundaries of the PU domains were reported. These coatings exhibited improved mechanical properties due to the reinforcing effect of the PU domains while retaining the low surface energy of the silicone elastomer. PU–silicone–hydrocarbon coatings with PDMS chains stopped with hydrocarbons in either loop or chain configurations or silicone-urethane coatings from curing of hydroxyl-terminated polyesters, isocyanates, and hydroxyl-terminated silicones were also reported as FRCs. They exhibited easy-clean properties and chemical and physical durability in field immersion.²⁷⁹ Cross-linked polysiloxane–polyurethane coating systems were also investigated in detail by Webster and co-workers^{202,280–285} as an alternative to silicone elastomer FRCs. Majumdar and Webster²⁸⁰ first synthesized cross-linked PDMS–polyurethane thick coatings that spontaneously showed a phase separation when using 10 wt % of PDMS, leading to microtopographical surface domains composed primarily of PDMS surrounded by a polyurethane matrix. This microtopographical surface was revealed to be stable upon water immersion because cross-linking enables stabilization of the system against rearrangement.²⁸⁰ The size and area distribution of the microdomains was shown to be controlled by the solvent used in preparing the coating and the time of mixing in solution prior to deposition.²⁸⁶ The presence of the surface microdomains was shown to decrease the adhesive strength of *A. amphitrite* barnacles.²⁸¹ Self-stratified cross-linked polysiloxane–polyurethane coating systems were further investigated to provide coatings that exhibit a soft,

rubbery top layer formed by the polysiloxane, with a tougher PU lower layer (Figure 27). During application and film

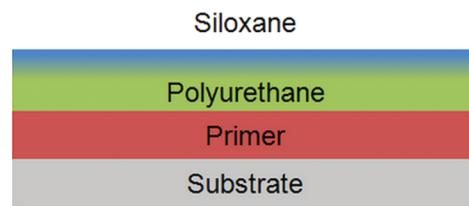


Figure 27. Self-stratified polysiloxane–polyurethane coating systems: the polysiloxane–polyurethane coating is applied in one step but spontaneously phase separated upon application and film formation.

formation, self-stratification occurs within the polysiloxane–polyurethane coating system, driven by the incompatibility of the polysiloxane and polyurethane components. This is reflected in the very low solubility parameter of polysiloxanes ($\delta = 14.9 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$) when compared to other polymers ($\delta = 17.6\text{--}28.6 \text{ J}^{1/2} \cdot \text{cm}^{-3/2}$).²⁸⁷ At the surface, phase separation is enhanced by the cooperative effects of surface energy minimization and hard and soft segment immiscibility.¹²⁹ In addition, the isocyanate group used to form the polyurethane may also react with residual hydroxyl groups on the epoxy anticorrosive primer that provided improved adhesion. Polysiloxane-PU coatings combine therefore toughness and good adhesion of PU as well as the low surface energy of polysiloxane to provide FR properties.

Combinatorial high-throughput approaches^{179,288–290} were developed for the synthesis of starting materials, and the coating formulation and characterization, thus accelerating the screening and down-selection of the candidates. The influence of the nature and the composition of the PDMS segment^{202,282} and the polyol²⁸³ and the influence of mixing time before deposition²⁸¹ on the surface and bulk properties and the resulting FR performances of cross-linked PDMS-PU systems were studied.

Fang et al.²⁹¹ demonstrated that the incorporation of poly(urea) segments to the PDMS backbone **54** (Chart 9) also gave rise to phase separation, with the extensively hydrogen bonded hard domains creating an interconnected network that imparts mechanical rigidity while retaining or enhancing the FR properties. Thermomechanical improvements were also provided by incorporating fluorinated **55** or polyhedral oligomeric silsesquioxane (POSS)-functionalized chain extenders **56** or through montmorillonite nanoclay intercalation. Despite the presence of polar urea linkages, all systems displayed a stronger hydrophobic character than a standard PDMS SilasticT2 and a higher CA hysteresis, which is related to their surface roughness. Compared to standard PDMS, all PDMS-poly(urea)-based coatings showed higher alga *Ulva* settlement but a better percentage removal of sporelings at pressures higher than 30 kPa. PDMS–poly(urea) coatings containing fluorinated groups **55** showed the best FR performance.

In addition to PU or poly(urea) modification, silicone-based FRCs were also modified with epoxy segments to improve their durability. An isocyanate-capped PDMS prepolymer was used to obtain silicone-modified aliphatic epoxy resins containing 15 and 30 wt % silicone content (**57**; Chart 10).^{292,293} The resulting films of these epoxy–silicone resins cured with a flexible polyetherdiamine cross-linker exhibited biphasic morphology. The coatings showed preferential segregation of

Chart 9. Hybrid Silicone FRCs Modified with Poly(urea) Segments

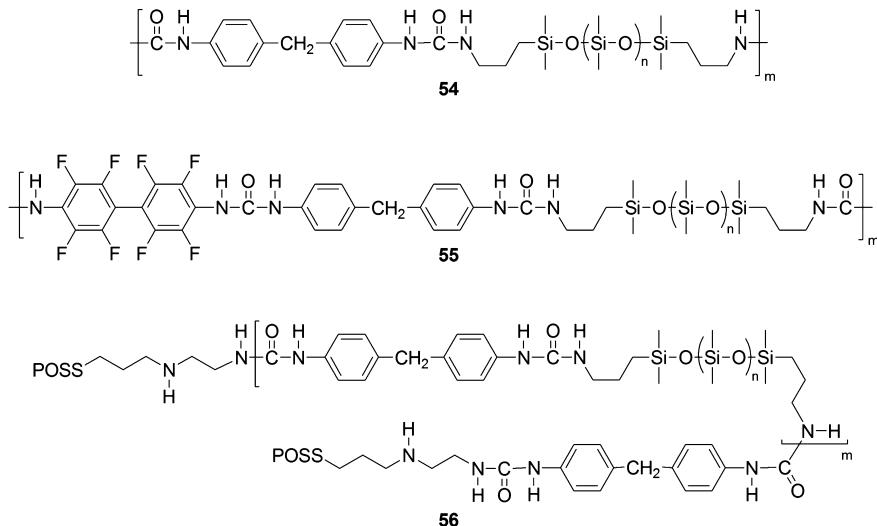
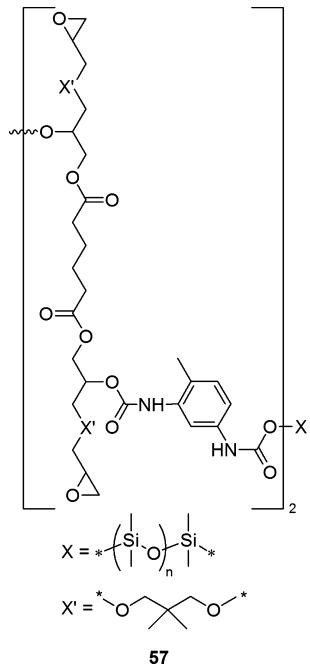


Chart 10. Hybrid Silicone FRC Modified with Polyurethane and Epoxy Segments

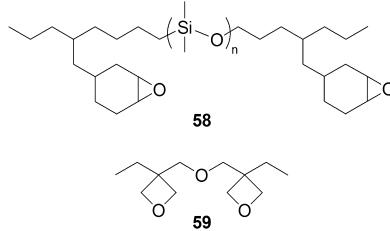


silicone moieties on the top surface, resulting in low surface energy and elastic modulus values. Their 1–2 MPa bond pull strength was reasonable in retaining the integrity of the coatings (adhesion of the coatings with the primer) to withstand the release of barnacles in shear mode. The 30 wt % silicone modified epoxy coating shows a pseudobarnacle adhesion strength of only 0.58 MPa, which is a reasonable value for a FRC (see section 4.1.1.3). However, the coatings suffered from surface reconstruction upon seawater immersion, with migration of epoxy and urethane moieties to the water surface. Consequently, the FR performance of the coatings decreased with *in situ* immersion time, with settlement of hard macrofoulants after 90 days.

Another potential alternative was to develop oxetane-toughened, UV-curable, epoxy-siloxane FRCs from photopolymerization of a cycloaliphatic epoxy-functionalized PDMS

resin 58 with a difunctional oxetane monomer 59 (Chart 11).²⁹⁴ 10- and 20%-oxetane coatings exhibited higher impact

Chart 11. Hybrid Silicone FRCs Modified with Epoxy Segments

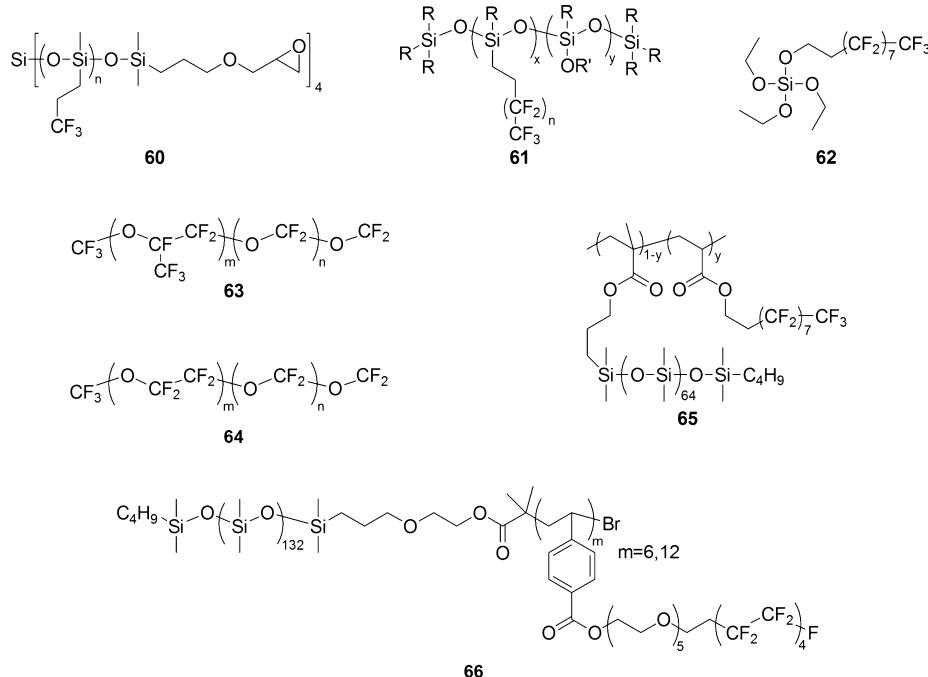


resistance than the 30% and 40% modified coatings. Their tensile modulus (40–50 MPa) was higher than those of silicone FRCs. Consequently, they behaved more like a hard thermoset polymer than a soft elastomer. These coatings had a low surface energy (<15 mJ·m⁻²), had a high water CA, and were stable after water immersion, with no surface reconstruction. The 10% and 20%-oxetane epoxy-siloxane coatings showed similar FR performances for bacteria *H. pacifica*, alga *Ulva*, and pseudo and live *A. amphitrite* barnacles compared to commercial silicone coatings. Thus, they appeared to be potential candidates for FRCs.

5.3. Silicone Coating Incorporating Fluoropolymers

Fluorinated compounds and polymers containing fluorinated moieties are known for their very low surface energy and hydrophobicity (see section 4.2.2), and several approaches have been attempted to improve the FR properties of silicone-based FRCs by the incorporation of fluorinated groups into the elastomeric silicone network. Grunlan et al.²⁹⁵ synthesized epoxy-terminated tetrabranched star oligofluorosiloxanes 60 (Chart 12) to generate cured films with α,ω -bis(3-amino-propyl)-terminated PDMS and phenolic-based catalysts. These films exhibited a high static water CA (99–117°) with similar *Ulva* sporeling removal to a control commercial FRC (Veridian), which makes them suitable materials to be used as FRCs. Mera and Wynne²⁹⁶ patented a FRC composition comprising a self-curable fluorinated silicone resin 61 cross-linked with a nonfluorinated organopolysiloxane resin. The

Chart 12. Hybrid Silicone FRCs Incorporating Fluoropolymers



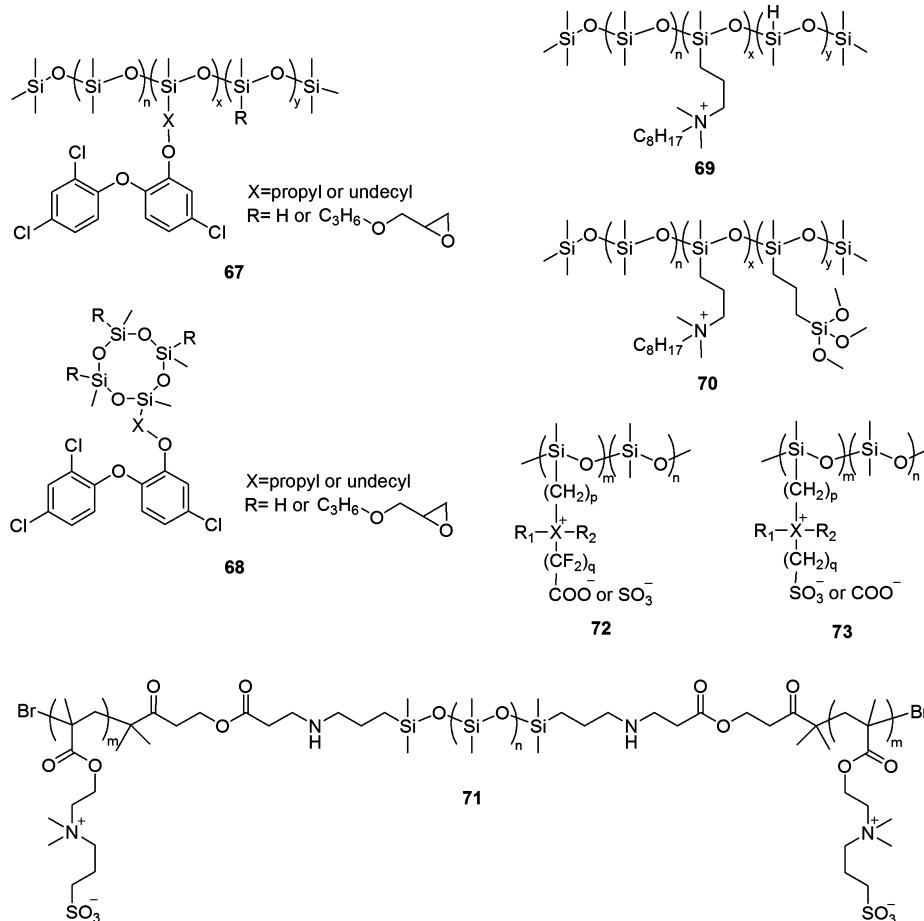
surface energies of such coatings were reported to be lower than those of pure silicone FRCs and to decrease with increasing amount of fluorine in the network. PDMS-based coatings containing 55% nonafluorohexyl ($\text{CF}_3-(\text{CF}_2)_8-$) moieties were *in situ* immersed for 15 months and showed fewer barnacles and less encrusting bryozoans settled than on the nonfluorinated PDMS control. However, the level of algal fouling was greater for the fluorosilicone. All fouling was shown to be easily removed from panels by wiping with a damp sponge. The fouling species that are typically harder to remove are barnacles and bryozoans. Very little bryozoans settled on the fluorosilicone, and barnacles that did settle were easier to remove from the fluorosilicone. With the PDMS control, some barnacles “undercut” the coating and attached directly to the underlying substrate; however, this did not occur with the fluorosilicone.²⁹⁶

Reactive perfluoropolyether polymers having an alkoxysilane end-group were also introduced in condensation-cured polysiloxanes to participate in the cross-linking reaction of the polysiloxane chains.²²¹ A fluorinated cross-linker such as (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (62) was used to cure α,ω -dihydroxy-PDMS instead of the conventional TEOS (13).²⁹⁷ The surface was then enriched by a fluorinated siliceous phase which increased the long-term hydrophobic stability of the coatings when they were exposed to water, compared to a standard PDMS elastomer cross-linked with 13. The coatings cured with 62 showed stable advancing and receding water CAs over a period of 3 months of water exposure, compared to a 70° decrease in receding CA for the TEOS-cured coatings. The fluorinated siliceous layer prevented the reconstruction of the polymer surface of the PDMS network.

From 2 to 10 wt % of unreactive fluorinated additive oils or fluids, including linear and trifluoromethyl-branched fluorine end-capped perfluoropolyethers (e.g., Fomblin Y 63), linear diorgano end-capped perfluoropolyethers (e.g., Fomblin Z 64), or polychlorotrifluoroethylenes, were added to a standard

condensation-curable PDMS to enhance its FR properties and stability in water.²¹⁶ After three months of immersion, the coatings accumulated significantly less fouling than the silicone FRC control. Blends of a fluorinated/siloxane acrylic copolymer 65 with a PDMS matrix were investigated to couple the low modulus character of PDMS with the low surface energy typical for fluorinated polymers.^{298,299} As the fluorinated copolymer had a lower surface energy than the PDMS matrix, it tended to segregate at the outer surface layer (~5 nm), at the air–coating interface. Thus, the addition of a fluorinated copolymer to PDMS allowed the coating surface to be fluorine-functionalized without affecting the mechanical properties of the bulk. Moreover, the fluorinated chain segments which formed a liquid crystal-like structure underwent microphase separation that was found to improve FR performance. Copolymers with a longer perfluorocarbon chain (eight CF_2 groups) exhibited a more pronounced tendency toward surface segregation than the one having a shorter chain (six CF_2 groups). Additionally, the surface-active fluorinated/siloxane copolymers were able to saturate the surface of the PDMS blend films even at very low loading (0.3 wt %), and the surface-segregated nanostructures were almost chemically the same after water immersion.²⁹⁸ These coatings were able to reduce the settlement of cyprid barnacles and exhibited higher release performance of *Ulva* sporelings and barnacles than pure PDMS.²⁹⁹ Further investigations were pursued where trimethoxysilylpropyl methacrylate was added as condensation-curable comonomer in chains composed of fluorinated (meth)acrylate and poly(dimethylsiloxane)oxypropyl (meth)acrylate monomer units 65. Then, the fluorinated/siloxane acrylic copolymer was able to participate in the curing reaction of a conventional PDMS-based paint composition, stabilizing the fluorinated surface layer formed by the migration of the fluorinated polymer at the polymer–air interface.³⁰⁰ Silicone FRC formulations including these fluorinated polymers were reported to have lower adhesion strength of pseudobarnacles in comparison with the silicone FRC without fluorinated

Chart 13. Hybrid Antifouling/Fouling Release Coatings



polymers. More recently, Martinelli et al.³⁰¹ synthesized amphiphilic diblock copolymers consisting of a PDMS block and a PEGylated-fluoroalkyl modified PS block **66** and investigated their use in blends (1–10 wt %) with a condensation-cured PDMS matrix. The block copolymers were designed to have a relatively long polysiloxane block to improve the dispersion of the copolymer itself in the elastomeric matrix, along with an amphiphilic modified polystyrene block to impart a low surface energy character. The coating surface presented a simultaneous hydrophilic and lipophilic character due to the strong surface segregation of the lowest surface energy fluoroalkyl chains of the block copolymer. All the blend coatings showed a 3- to 14-fold improvement in release of *Ulva* sporelings compared with the PDMS control.

5.4. Hydrogel Silicones

As previously described, silicone FRCs are mainly affected by the settlement of diatoms, since hydrophobic surfaces seem to favor the adhesion of such fouling organisms.²⁵ To overcome this problem, Hempel developed a further generation of FRCs through a “hydrogel silicone” approach.³⁰² Hydrogels are cross-linked polymeric structures containing either covalent bonds or physical cross-links from entanglements, association bonds such as hydrogen bonds, or strong van der Waals interactions between chains.³⁰³ These hydrophilic polymer networks are water-insoluble, but they can be swollen and absorb over 99% of their original weight of water. Hydrogels are commonly used in medical applications, as they are well-known to minimize protein and bacterial adhesion. Hydrogels were first used

during the development of poly(2-hydroxyethyl methacrylate) gels as soft contact lens materials in the late 1950s. Today, hydrogels are used in numerous biomedical applications, including ophthalmological devices, biosensors, biomembranes, and carriers for drugs or protein-controlled delivery.³⁰³ More recently, several studies explored the potential use of hydrogels for fouling control purposes.^{304–307} For example, Rasmussen and Østgaard³⁰⁴ tested various gels against marine bacterial adhesion, finding best results with a modified poly(vinyl alcohol) gel. Hydrogels containing PEG were shown to exhibit promising fouling resistance and FR properties against various marine fouling organisms, such as marine bacteria, diatoms, alga, and barnacles.^{306,307}

Hempel combined the hydrogel aspect with the previous silicone FRC technology through the commercial HempsilX3 paint. Their hydrogel-modified silicone FRC maintains a more hydrophilic surface which delays the settlement of diatomic slime compared with silicone FRC. Indeed, due to a certain, controlled, immiscibility, the hydrogel polymers have a tendency to slowly phase-separate to the PDMS–water interface. Once in contact with water, they become hydrated and impart a certain hydrophilic character to the otherwise hydrophobic matrix and additives ($\theta_w = 96^\circ \pm 1^\circ$ compared with $\theta_w = 104^\circ \pm 1^\circ$ for traditional FRC).³⁰² Moreover, the PDMS matrix also serves as reservoir for hydrogel precursors which self-regenerate the hydrogel surface layer if it is damaged through, for example, mechanical abrasion.³⁰² The efficiency of hydrogel-based FRCs has been demonstrated by high-throughput screening techniques²⁹⁰ on soft fouling organisms

(bacteria *C. lytica* and diatom *N. incerta*) and hard fouling organisms (barnacle *A. amphitrite*).¹⁰⁶ Moreover, the hydrogel segregation at the surface of the coating leads to a lower hull skin friction over longer periods of time, which contributes to significantly lower fuel consumption. Indeed, friction coefficients of gels are generally much lower than those of solids, which is related to the high water content of the hydrogel network.³⁰⁸

5.5. Hybrid Antifouling/Fouling Release Coatings

Several studies dealt with the development of marine coatings which involved combining characteristics of a biocidal AF coating with the characteristics of a FRC by incorporating biocides in silicone coatings. A new marine coating that contained a nonleaching/nonmetallic biocide was developed where Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) was covalently attached to the siloxane backbone.^{309–312} Triclosan is a broad spectrum antibacterial/antimicrobial agent used in various personal care and consumer products such as shampoo, deodorants, and toothpaste. Such AF/FR coatings were synthesized by covalently bonding alkylene-modified Triclosan and glycidyl ether to a poly(dimethyl-co-methylhydrosiloxane) (**67**) or a cyclic methylhydrosiloxane (**68**) backbone (Chart 13).³¹³ This modified siloxane was then cured using a vinyl-terminated PDMS for the hydrosilyl functionality and 1,3-cyclohexane-bis(methylamine) for the epoxy cross-linking functionality. The resulting coatings exhibited high water CAs ($>90^\circ$) and low surface energy ($<30 \text{ mJ}\cdot\text{m}^{-2}$). The coatings with moduli in the range of 0.1–10 MPa were soft enough for biocide migration to the surface, so as to provide a biocidal surface, and showed significant reduction in barnacle recruitment. For high modulus coatings, the biocide could be trapped in the highly cross-linked polymer matrix and was unable to easily migrate to the surface to prevent macrofouling settlement, whereas barnacles appeared to cut through the very low modulus coatings ($<0.1 \text{ MPa}$) and grow on the anticorrosive primer. A similar study dealt with the incorporation of (meth)acrylate monomer bearing a Triclosan moiety into a silicone matrix made of vinyl- and methacryloxypropyl-terminated PDMS cured with a polyhydrosiloxane-based curing agent.³¹⁰ The coatings showed high water CAs ($>105^\circ$) and low tensile modulus ($\leq 1.6 \text{ MPa}$). From static immersion studies, the coatings incorporating acrylate Triclosan performed almost as well as the Cu-based ablative coating reference for the early stage of immersion (29 days of immersion), and their FR performance (estimated from the adhesion strength of barnacles) was comparable with a commercial FRC reference (Intersleek 425). However, they became more heavily fouled after 85 days of immersion.

Cross-linked polysiloxane coatings containing tethered quaternary ammonium salt (QAS) moieties were investigated for use as environmentally friendly AF/FRCs.³¹⁴ QASs have already been indexed as biocides.³¹⁵ In particular it was proven that QASs having an alkyl chain with at least eight carbons are effective biocides.³¹⁶ QAS-containing polymers have been shown to have biocidal activity against several species of marine algae³¹⁷ and a relative resistance to microfouling in seawater immersion.³¹⁸ QAS-functionalized PDMS **69** cured by hydrosilylation were first synthesized.³¹⁴ However, increasing the QAS concentration to obtain good reduction in biofilm retention yielded to poor film stability upon seawater immersion due to excessive swelling. As a result, these studies were continued using moisture-cured QAS-functionalized

polysiloxanes, which enabled the formation of networks with a higher cross-link density and reduced swelling by water absorption. A moisture-cured QAS-functionalized PDMS coating containing 29 wt % QAS moieties allowed for very high biocidal activity without leachate toxicity and excellent film stability upon seawater immersion. A high reduction of biofilm retention was obtained for the bacteria *C. lytica* and the diatom *Navicula incerta*.³¹⁴ Blends of a silanol-terminated PDMS in solution with a QAS-functionalized alkoxy silane **70**, and methyltriacetoxysilane as cross-linker, were widely investigated using combinatorial/high-throughput experiments.³¹⁹ The concentration of the QAS-functionalized alkoxy silane, the length of the alkyl chain attached to the nitrogen atom (R₁ in Figure 28), and the molecular weight of the silanol-

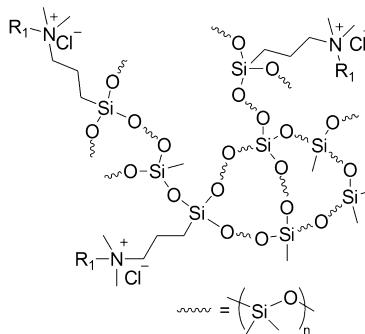


Figure 28. General structure of QAS-functionalized PDMS resulting from the reaction of a QAS-functionalized alkoxy silane **70**, a silanol-terminated PDMS in the presence of methyltriacetoxysilane as cross-linker.

terminated PDMS^{319,320} as well as the alkoxy silane functionality of the QAS-functionalized silane³¹⁹ were compositional variables which could affect the FR performances.

The hydrophobicity of such coatings was shown to increase with increasing QAS concentration.³²⁰ Coatings exhibiting an AF effect and/or enhanced FR properties generally possessed a heterogeneous surface morphology with segregation of QAS groups to the coating–air interface. Higher concentrations of QAS-moieties at the surface were obtained when they were functionalized with ethoxysilane rather than methoxysilane due to a slower cross-linking reaction rate, which allows more time for diffusion of the QAS-functionalized silane to the coating–air interface.³¹⁹ From the investigation of tens of coatings using combinatorial/high-throughput experiments, the coating containing a hexadecyl ammonium salt exhibited the best performance, with lower settlement and higher removal of microfouling species such as *C. Lytica*, *H. pacifica*, and *N. incerta* compared to the commercial FRCs Intersleek700 and 900 and Silastic T2. In addition, the biomass that was retained was essentially completely removed by water-jetting. Majumdar et al.³²¹ also demonstrated that the modification of a polysiloxane matrix with QAS groups, coupled with the addition of silica nanoparticles, may provide a novel means for improving the toughness and durability of silicone FRCs. The ionic groups present in the PDMS-QAS matrix provide increased interfacial adhesion between the polymer matrix and silica particles, which is attributed to ion–dipole interactions involving silanol groups present on the silica surface. The enhanced adhesion enabled major increases in modulus, tensile strength, and toughness compared to the unfilled matrix as well as to the nonionic, silica-filled analogue.

Another approach to design AF/FRCs is the use of zwitterionic silicone coatings. Zwitterionic polymers are polymers having a balance of positive and negative charges. Due to their biomimetic nature, zwitterionic polymers, such as phosphobetaine, sulfobetaine, and carboxybetaine polymers, could be highly resistant to protein adsorption and bacterial adhesion, exhibit biocompatibility, and are environmentally benign.³²² Recently, Webster et al.³²³ reported the synthesis of zwitterionic/amphiphilic pentablock copolymers **71** and their use as reactive additives in a PU-based coating, resulting in an amphiphilic AF/FRC. The pentablock was synthesized by atom transfer radical polymerization from a PDMS-PEG-Br macro-initiator and sulfobetaine methacrylate, and it was further incorporated into a polyol-polyisocyanate PU coating composition. The PDMS component was able to self-stratify to the coating surface, bringing the chemically bound protein-resistant polymers to the surface as well. Thus, the hydrophilic polymer segments were concentrated on the surface. During the curing process, the pentablock copolymer was able to react with the isocyanate groups of the cross-linker *via* secondary amine groups at the junction of the PDMS and PEG segments while forming a cured coating. The surface of the amphiphilic pentablock copolymer-containing PU coating was shown to be initially hydrophobic as a result of the stratification of the pentablock containing PDMS to the coating surface. Upon contact with water, the hydrophilic components of the pentablock copolymer migrated to the surface, which illustrates the amphiphilic behavior of such a PU coating. Evaluated against various organisms including bacteria, diatoms, and pseudobarnacles, these coatings demonstrated better or similar AF and FR properties than silicone standards or commercial silicone FRCs. Jiang et al.³²² patented other zwitterionic/amphiphilic silicone-based polymers that contain a cationic center and hydrolyzable groups that provide zwitterionic polymers through hydrolysis. These polymers may also contain perfluoroalkyl pendant groups to the silicone main chain (**72–73**). These polymers were claimed to have amphiphilic characteristics with good AF and FR properties.

6. CONCLUSIONS AND FUTURE TRENDS

Antifouling coatings are essential for preventing the growth of fouling on immersed structures. Two main technologies are available: biocide-based coatings which inhibit fouling settlement by release of biocidal products into the marine environment, and nontoxic fouling release coatings whose antifouling efficiency rely on the low adhesion strength and easy release of fouling organisms on such a coating. Since the ban of TBT-based AF coatings, the amount of legislation concerning the use of biocides is intensifying. Even if biocide-based AF coatings still represent the main part of the AF coatings market, FR coatings based on silicone are expanding, as they do not contain biocides and, moreover, enable savings in fuel costs. Research in the academic and industrial domains is intensifying to improve the efficiency of FRCs against slime fouling and to develop coatings with FR ability at low speed or during idle periods, particularly with the development of fluorobased polymers and hybrid FR coatings. For the moment, FRCs are not subjected to biocidal legislation, but some concern over additive oils may arise in the future. Within the context of worldwide pressure for legislation limiting the use of biocides, and ever-increasing fuel prices, FRCs are now considered to be the most promising environmentally friendly antifouling technology.

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Notes

The authors declare no competing financial interest.

Biographies



Marlène Lejars was born in 1986 in Gennevilliers, France. In 2009, she graduated from the National School of Chemistry, Biology and Physics (ENSCBP) of Bordeaux and received a Master degree in Chemistry (Polymers and Colloids) from Bordeaux 1 University. Currently, she is pursuing a Ph.D. degree in Chemistry at the University of Toulon, France, under the supervision of Dr. Christine Bressy and Prof. André Margaillan at the “MAtériaux Polymères Interfaces Environnement Marin” (MAPIEM) laboratory. The main focus of her work is developing well-architected copolymers with hybrid antifouling/fouling release properties.



André Margaillan was born in Morelia, Mexico, in 1958. He obtained his Ph.D. degree in 1987 at the University of Marseille I, working under the direction of Professor J. L. Vernet on the mechanism of action of antifouling coatings. In 1992, he obtained a postdoctoral position in the laboratory of Professor Thieo Hogen-Esch (University of Southern California, U.S.A.). There he worked on the synthesis of block copolymers through anionic polymerization. In 1993, he obtained a position of Professor at the University of Toulon. He developed a team dealing with macromolecular engineering. The main domain of application was antifouling coatings and drag reduction agents. Since 2007, he has managed the “MAtériaux Polymères Interfaces Environnement Marin” (MAPIEM) laboratory.



Christine Bressy obtained her Ph.D. degree in 1996 at the University of Montpellier, France (Laboratory of Applied Chemistry, Prof. B. Boutevin as supervisor), working on the synthesis of phosphonated monomers and copolymers for anticorrosive coatings. Following her Ph.D., she was appointed in the team of Prof. A. Margaillan (1996–date) at the University of Toulon, France, to work on polymer coatings and, more specifically, on antifouling coatings. There, Dr. Bressy worked on the development of new tin-free acrylic binders for self-polishing marine paints including polymers containing tertiary ammonium salts and polymers containing silylated side-groups. Currently, she works on the development of new antifouling paints that have lower impact on the environment and that are efficient over a long term period. She is involved in several projects: the ECOPAINT project (2007–2011); a European Defence Agency project with European navies (Antifouling Coatings for War Ships, 2008–2011). Dr. Bressy is also involved in testing and expertise proposals to industrial customers in the antifouling paint area.

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GLOSSARY

AF	antifouling
ASTM	American Society for Testing and Materials
BA	butyl acrylate
BMA	butyl methacrylate
CA	contact angle
CDP	controlled depletion copolymer
FR	fouling release
FRC	fouling release coating
HBPF-PEG	hyperbranched polymers with fluorinated and PEGylated groups
HEA	hydroxyethyl acrylate
MWCNT	multiwall carbon nanotube
PA	polyacrylate
PDMDPhS	poly(dimethyldiphenylsiloxane)
PDMS	poly(dimethylsiloxane)
PEG	poly(ethylene glycol)
PEG-MA or -DMA	mono- or dimethacryloxy-PEG macro-monomers
PFPE	perfluoropolyether

PMMA	poly(methyl methacrylate)
POSS	polyhedral oligomeric silsesquioxane
PS	polystyrene
PS-PI	poly(styrene)- <i>b</i> -poly(isoprene) block copolymer
PS- <i>b</i> -P(E/B)- <i>b</i> -PI	poly(styrene)-block-poly(ethylene- <i>ran</i> -butylene)-block-poly(isoprene)
PTFE	poly(tetrafluoroethylene)
PU	poly(urethane)
PVC	poly(vinylchloride)
QAS	quaternary ammonium salt
SABC	surface-active block copolymer
SBMA	sulfobetaine methacrylate
SEBS	styrene-ethylene/butylene-styrene tri-block copolymer
SPC	self-polishing copolymer
SS	styrenesulfonic ester monomer
TBT	tributyl tin
TEOS	tetraethoxysilane
T _g	glass transition temperature
sPFPE	distyrenyl-modified PFPE

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