Functional polymer materials for modern marine biofouling control

Qiu, Haoyi; Febg, Kang; Gapeeva, Anna; Meurisch, Kerstin; Kaps, Sören; Li, Xia; Yu, Liangmin; Mishra, Yogendra Kumar; Adelungd, Rainer; Baum, Martina

Published in:
Progress in Polymer Science

DOI:
10.1016/j.progpolymsci.2022.101516

Publication date:
2022

Document version:
Final published version

Document license:
CC BY

Citation for published version (APA):

Go to publication entry in University of Southern Denmark's Research Portal

Terms of use
This work is brought to you by the University of Southern Denmark. Unless otherwise specified it has been shared according to the terms for self-archiving. If no other license is stated, these terms apply:
- You may download this work for personal use only.
- You may not further distribute the material or use it for any profit-making activity or commercial gain.
- You may freely distribute the URL identifying this open access version.
If you believe that this document breaches copyright please contact us providing details and we will investigate your claim. Please direct all enquiries to puresupport@bib.sdu.dk

Download date: 08. Jun. 2023
Functional polymer materials for modern marine biofouling control

Haoyi Qiu\textsuperscript{a,b,1}, Kang Feng\textsuperscript{a,c,d,1}, Anna Gapeeva\textsuperscript{a}, Kerstin Meurisch\textsuperscript{a}, Sören Kaps\textsuperscript{a}, Xia Li\textsuperscript{c}, Liangmin Yu\textsuperscript{c}, Yogendra Kumar Mishra\textsuperscript{e}, Rainer Adelung\textsuperscript{a,e}, Martina Baum\textsuperscript{a}

\textsuperscript{a} Functional Nanomaterials, Institute for Materials Science, Faculty of Engineering, Kiel University, Kaiserstr. 2, D-24143 Kiel, Germany
\textsuperscript{b} Phi-Stone AG, Kaiserstr. 2, D-24143 Kiel, Germany
\textsuperscript{c} Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, 266100 Qingdao, China
\textsuperscript{d} Marine Science and Technology College, Zhejiang Ocean University, 316022 Zhoushan, China
\textsuperscript{e} Mads Clausen Institute, NanoSYD, University of Southern Denmark, Alson 2, 6400 Sønderborg, Denmark

\textbf{A R T I C L E   I N F O}

Article history:
Received 30 June 2021
Revised 28 December 2021
Accepted 25 January 2022
Available online 29 January 2022

Keywords:
Polymer materials
Biofouling
Antifouling
Fouling-release
Marine coatings

\textbf{A B S T R A C T}

Marine biofouling is a well-known massive problem: within the shortest time, ship hulls and other man-made submerged surfaces are inevitably populated by various marine organisms. Marine biofouling causes severe economic and environmental problems. Thus, effective biofouling control on submerged surfaces is of utmost importance. Since the middle of the 20th century, scientists and engineers have developed antifouling coatings mainly based on the continuous release of toxic metal ions and accompanying booster biocides to repel or kill organisms approaching the surface. However, these coatings caused serious harm to non-target organisms and the ocean. Therefore, the development of environmentally friendly alternative coatings is an urgent need, and research in this field is growing rapidly. This review includes concise basic theory from biology, chemistry, and physics. It provides an introduction into the biofouling formation, as well as physicochemical surface properties that can be manipulated to achieve an effective biofouling control. Furthermore, a complete overview of the currently developed biofouling control coatings is presented and summarized. This overview includes coatings based on surface wettability, self-renewable coatings, coatings containing antifouling agents, switchable coatings, and biomimetic coatings.

© 2022 The Author(s). Published by Elsevier B.V.
This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/)

1. The modern dilemma of marine biofouling control coatings

The problem of biofouling, the growth of micro- and macroorganisms on submerged surfaces, such as ship hulls or propellers, has been known since the invention of shipping in ancient times. Today, it becomes more and more urgent, yet its prevention remains a challenging and controversial topic. The modern dilemma of marine biofouling control coatings (Fig. 1) can be summed up as follows:

(i) On the one hand, biofouling causes dramatic economic and energetic losses, together with several serious ecological problems, and must be prevented.

(ii) On the other hand, most of the commonly used, more traditional coatings are toxic and can cause severe environmental problems.

\textsuperscript{1} Corresponding authors.
E-mail address: mishra@pnci.sdu.dk (Y.K. Mishra).
\textsuperscript{1} Shared first authorship.
Fig. 1. The modern dilemma of biofouling control – historical development and future trends. On the one hand, biofouling causes problems that are not tolerable. On the other hand, the commercially available biofouling control coatings still have significant drawbacks. The historical development implies that the future in this field lies in biofriendly solutions.

damage. Additionally, alternative, modern, and biofriendly coatings are still less effective and not widely used.

This section provides a look into the negative economic and environmental impact of biofouling film formation, as well as the historical development of its countermeasures. It will help to rank the advantages and risks of biofouling control coatings and introduce future trends, which will be reviewed in detail in Sections 4–8.

Economic losses are a major part of the problems caused by biofouling. Since biofouling roughens the surfaces and causes increased frictional resistance and drag, it reduces the speed and maneuverability of a ship. Calculations of power requirements needed to overcome the extra drag and maintain the operational speed showed that even a low degree of biofouling in the form of a light slime film increases the required shaft power up to 11% [1]. In contrast, heavy calcareous fouling results in powering penalties up to 86% [1]. Schultz et al. (2011) calculated that a high degree of fouling on a mid-sized naval ship caused an increase of 20.4% in fuel consumption compared to an unfouled hull with a smooth surface [2]. The Naval Surface Warfare Center at Carderock (USA) estimated an even higher increase of fuel consumption up to 40% as a result of added resistance due to biofouling [3]. Nowadays, where more than 80% of global trade by volume is carried out by shipping [4], these effects can cause huge financial losses due to increased operating fuel costs, more frequent docking times, as well as intensive personal and machinery efforts. For instance, for the DDG-51 class of naval vessels, a large ship with a length of about 150 m, constituting up to 30% of the US fleet, the overall expenses associated with hull fouling were estimated to be approximately $56 M per year or $1.0 B over 15 years, with costs for increased fuel consumption being the largest source of costs [2].
Next to these economic considerations, environmental aspects are getting more and more attention. Increased fuel consumption caused by biofouling leads to additional CO$_2$ as well as NO$_x$ and SO$_x$ emissions, having negative effects on climate protection and increasing the generation of fine dust, negative health implications, and acid rains [5]. Moreover, the migration of non-native species on ship’s hulls as biofouling is one of the major risk factors of bio-invasions threatening the indigenous biodiversity [6].

However, in the first place, it was probably mainly due to the economic losses, that humans were eager to develop preventive strategies against biofouling. The historical development of these strategies reflects the scientific progress in parallel to the evolution of shipping transportation. For some generations now, the upcoming environmental awareness induces further development. One of the dramatic stories in the 20th century is the rise and fall of tributyltin (TBT) containing ship coats (Timeline in Fig. 1, and Section 1.1). At that time, several technological developments in the field of chemistry helped to create more and more powerful antifouling. That means biofouling control coatings are so toxic, that any growth on them could be prevented effectively. Yet, due to their extensive use and the vast increase of shipping transportation, their environmentally harmful properties were soon uncovered. This is why, at the end of the 20th century, strongly toxic coatings were restricted or prohibited in many countries, and researchers came up with biofriendly alternatives using natural biocides or fouling release technology (Timeline in Fig. 1, and Section 1.2).

1.1. Rise and fall of toxic antifouling coatings

The upcoming of container shipping in the late 1950s led to a revolution in cargo transportation and a rapid expansion of the international economy between 1950 and 1973, known as The Golden Age [7]. At approximately the same time, biocidal properties of organotin compounds, like TBT, were discovered. TBT containing antifouling paints rapidly conquered the market due to their high long-term effectiveness, which provided major economic advantages for commercial as well as recreational shipping. Hence, being applied to all vessel types, from small private yachts to large container ships and tankers, TBT was spread globally in large amounts. However, it was soon realized that the release of TBT and co-biocides contained in the antifouling paint formulations was harming the aquatic environment by contaminating the waters and accumulating in non-target organisms. In the late 1970s and early 1980s, oyster cultures in Arcachon Bay (France) suffered from severe shell deformations, growth impediments, and reproductive failure. This caused not only a drastic reduction of oyster market value but also led to a complete loss of oyster larvae (spat) needed for oyster cultivation and resulted in serious financial losses for shellfish farms [8]. Laboratory and in-situ studies showed that TBT released from leisure boats in the nearby marinas was responsible for shell abnormalities, as well as inhibited growth and survival of Crassostrea gigas oyster larvae [9]. A strong correlation between the use of TBT and the development of male sex organs in addition to female ones (“imposes”) in marine gastropods (Nucella lapillus, or dog whelk) was drawn in numerous studies conducted in the UK and attributed to the interference of TBT with the endocrine system of mollusks [10,11]. After the introduction of partial restrictions prohibiting the use of TBT on small boats, rapid recovery of oyster conditions was observed in France and the UK [12,13]. Similarly, restoration of marine gastropod populations was reported [14]. Despite a series of national restrictions on TBT usage for small boats around the world, the continued application of TBT containing antifouling paints on commercial ships led to a ubiquitous presence of TBT in the sediments, flora, and fauna of the world’s oceans, and remains a challenge for marine ecosystems. As a result, in 2008, the use of TBT antifouling paints was globally prohibited by the International Maritime Organization [15].

This development finally led to a revival of antifouling systems based on copper, whose biocidal properties have been known since the 17th century and have been used until the breakthrough of TBT. Copper-based paints mainly contain cuprous oxide (Cu$_2$O), cuprous thiocyanate (CuSCN), or metallic copper as a biocide [16]. Contact with water leads to the formation of copper ions (Cu$^{2+}$), which are responsible for a toxic environment in close proximity to the coating. As copper ions diffuse from the surface, they mostly become neutralized through organic and inorganic ligand interactions, reducing toxic effects away from the surface [17]. Nevertheless, first concerns regarding the safety of alternative formulations due to the lack of toxicity data and evaluation of potential risks for non-target marine organisms were raised even before the new regulations came into force [18]. In the Bay of Arcachon, where the use of TBT was banned already in 1982 and copper-based paints were used instead, an increase of the copper content in oysters was observed [19]. In 1986, mortal effects of high concentrations of copper on C. gigas oysters were reported in the coastal area in Taiwan [20]. Brown algae Fucus vesiculosus was shown to be most sensitive to copper during germination. Unfortunately, high season and therefore increased copper release from leisure boats in the Baltic Sea coincides with the release time of gametes and therefore significantly affects the fertilization and germination of F. vesiculosus, which can lead to a change in its genetic diversity [21]. Copper was also found to be genotoxic to polychaeta Alitta virens at concentrations present in the sediments in coastal regions [22].

Still, copper is only part of the problem: Since some algal groups (e.g., Enteromorpha, Ectocarpus, Achnanthes) are resistant to copper, in order to effectively prevent all kinds of biofouling, antifouling paints are supplemented by so-called “booster” co-biocides, such as herbicides commonly used in agriculture [16]. The broad-spectrum effect impact of booster biocides on the marine ecosystem raises considerable environmental concerns as well. Early warnings were already expected at the beginning of the 1990s, when extremely high levels (up to 1700 ng/L) of the agricultural herbicide IRGAROL 1051 were discovered in Cote d’Azur coastal waters in France [23]. Later, the presence of antifouling booster biocides such as IRGAROL 1051, Diuron, Sea-Nine 211™, Dichlofluanid, Chlorothalonil, and others in the aquatic environment was reported worldwide [24]. Concentrations of IRGAROL 1051 significantly lower than those found in contaminated areas were shown to be toxic to phytoplankton and periphyton communities [25,26]. Accumulation and/or interaction of booster biocides was found to affect the growth of non-target algae and to cause the development of tolerance of marine microbial communities against the toxicant [27,28]. This can have serious ecological consequences, such as a loss of diversity and a reduction of antifouling paint effectiveness.

Nowadays, all biocide-containing antifouling paints are facing strict regulations regarding the release rate and must undergo a registration process. For example, to place a biocide containing antifouling paint on the European market, it must be approved according to the Biocidal Products Regulation (EU) No 528/2012 [29]. Therefore, even though copper-based antifouling paints offer adequate protection against biofouling, due to increasing signs of the negative impacts on the marine ecosystem, their future is undefined and may befall the same fate as TBT.

1.2. Biofriendly fouling control technologies

The challenge to prevent biofouling formation effectively, without introducing toxic substances into the aquatic environment, has driven research to develop alternative, biocide-free technologies.
Especially one approach has been intriguing scientists since the 1980s: This is to design a “non-stick” coating that would make it impossible for marine organisms to attach to a hull [30,31]. However, it is an extremely difficult task to find such a universal coating due to a huge diversity of adhesion mechanisms varying within and with the type of fouling organism (Section 2) and with geographic location and seasonal changes (like salinity, clarity, temperature, and available micronutrients) [32]. One of the main approaches in this direction is the so-called fouling-release technology, based on the idea that microorganisms adhere poorly to substrates with low surface free energy and can therefore be easily removed if shear forces are acting on the surface, e.g., during movement of a ship or a cleaning procedure (Fig. 1). The fouling-release effect is enhanced if nano- or microscale roughness is added on the surface, which leads to a superhydrophobic behavior in the Cassie-Baxter wetting regime [33]. Fouling-release coatings are mostly based on fluoropolymers such as polytetrafluoroethylene (PTFE) or siloxanes (mostly designated as silicons) such as polydimethylsiloxane (PDMS). Silicons are considered more advantageous in terms of fouling release properties due to a lower elastic modulus, which enables mechanical deformation under stress and thus, an easier crack propagation mechanism similar to the peeling process [34]. However, if used alone, silicone suffers major drawbacks, such as low adhesion to substrates, susceptibility to mechanical damage as well as poor antifouling behavior under static conditions. The latter is associated with non-specific protein adsorption due to the intrinsic hydrophobicity of silicone, which gives rise to a formation of biofilm and subsequent biofouling formation requiring higher shear forces for release. A large variety of composite materials was developed to overcome these disadvantages, as reviewed in Section 4.1.

Furthermore, as numerous organisms exhibit promising antifouling performance (e.g., sharks, pilot whales, certain plants, etc.), researchers have been trying to fabricate environmentally friendly fouling control coating by incorporating bioactive substances from organisms as an antifouling agent or by imitating the physicochemical surface properties of these organisms (Sections 6 and 8, respectively). However, the fabrication of such surfaces on a large scale or the extraction of active substances in a high amount is still challenging. In a nutshell, there is still much work to be done for materials scientists and biologists to develop effective and yet biofriendly biofouling control coatings. This article provides a concise theoretical introduction about marine biofilm formation (Section 2) as well as the physicochemical factors which can be manipulated to weaken the organisms’ adhesion (Section 3). Finally, Sections 4–8 reviews the progress made in the field of modern and biofriendly marine biofouling control coatings. This review is focused on the academic development of the biofouling control polymer materials in recent years, while the industrial coatings (e.g., Intersleek) will not be discussed in this review. Fig. 2 gives a first overview of the different, modern approaches in biofouling control. Please note that most of these coatings are multifunctional and usually cannot be classified into only one group of control mechanisms. Nonetheless, these coatings are generally summarized into five categories based on their main biofouling control mechanisms, i.e., coatings based on unfavorable surface wettability, self-renewable coatings, coatings containing antifouling agents, stimuli-induced switchable coatings, and biomimetic coatings.

2. Marine biofouling formation

Marine biofouling describes the unwanted accumulation of microorganisms, algae, and other organisms on artificial surfaces submerged in seawater [35]. The formation of biofouling on solid surfaces is a very complex process, and over 4000 organisms are related to the marine biofouling problem [36]. According to Dobretsov [36] and as depicted in Fig. 3, four main phases can be distinguished during the development of biofouling:

(i) In the first seconds after immersion, the formation of a conditioning film is initiated by adsorption of inorganic and organic macromolecules (mostly proteins);
(ii) In the next few hours, transport of microbial cells to the surface occurs, and a so-called primary film is generated, which is characterized by an irreversible attachment of bacteria and production of adhesive extracellular polymeric substances [37];
(iii) On a time scale of a week, multi-cellular species, such as spores of macroalgae and protozoa, arrive at the surface, which are parts of microfilm;
(iv) Finally, the formed microfouling film stimulates the recruitment of animal larvae, such as barnacles and mussels, which belong to macrofouling [38].

Although the model of biofouling formation described above is generally accepted by researchers, it suffers from an oversimplification [39]. The phases do not necessarily follow strictly one after another, but may instead overlap or take place in parallel. There is no universal agreement on the exact timeline of the settlement of different organisms. For example, it was shown that larvae of some barnacles or bryozoans can settle on the surface even before the formation of microfilm [38,40]. However, concerning the huge amount of species involved, there is a consensus that among the more than 4000 known fouling organisms worldwide, only 10 types of microorganisms (bacteria, diatoms, and algae spores) are considered as the most common microorganisms. Barnacles, tuberculosis worms, bryozoans, mussels, and algae are the main macroorganisms associated with biofouling [34,35]. As summed up in Table 1, each of these species follows its unique attachment strategy. The complexity of attachment mechanisms, as well as the high variety of factors affecting biofouling formation, makes it impossible to derive a universal strategy for marine biofouling prevention [38]. Nevertheless, when studying common attachment processes, it quickly becomes clear that effective biofouling control either has to directly hinder primary attachment (antifouling strategy) or permanently weaken the adhesion to facilitate release or cleaning (fouling-release strategy). As will be discussed in Section 3, the key to successful biofouling control lies within the coating’s surface properties, such as surface free energy, topography, wettability, and chemical activity.

3. Coating properties affecting the biofouling formation

There are many factors that influence the biofouling formation on solid surfaces: environmental conditions (temperature, pH, etc.), interfacial interactions (surface charge, surface free energy, chemically active components, etc.), and physiological factors (microorganism type, growth stage, metabolic activity) [84,85]. However, among these factors only interfacial interactions can be manipulated in order to control or to prevent the biofouling formation on man-made surfaces [85]. Therefore, taking advantage of the optimized surface properties such as low surface free energy or nanorough topography of a coating to achieve biofouling control effects has become more and more essential and relevant in recent years [86,87].

The adhesion of bioorganisms on submerged surfaces originates from mechanical interlocking and/or intermolecular interactions. Intermolecular interactions can be chemical, dispersive, electrostatic, or diffusive. The adhesion strength depends on the type of surface interaction, the joint failure mechanism, and the total area involved. As illustrated in Fig. 4, there is a variety of surface properties of a coating that can be designed to control the biofouling formation at its different growth stages.
Fig. 2. Overview of the modern approaches to an alternative and biofriendly marine biofouling control. [The here used figures have been adapted with permission from published papers cited in this review.]

Fig. 3. Complexity of the biofouling formation process: The biofouling formation as a whole evolves with time, which makes it extremely challenging to develop a universal biofouling control technique accounting for the different species and stages in the process.
### Table 1
Summary of the different attachment processes and strategies of typical biofouling organisms.

<table>
<thead>
<tr>
<th>Biofouling species</th>
<th>Attachment process and strategies</th>
<th>Notes</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfouling</td>
<td>Bacteria</td>
<td>Primary attachment via physicochemical interactions (van-der-Waals, electrostatic, hydrophobic, etc.); Secondary attachment via molecular interactions (capsules, fimbriae, slime)</td>
<td>A highly complex process strongly depending on the surface properties of the bacterium</td>
</tr>
<tr>
<td></td>
<td>Proteins</td>
<td>Non-covalent interaction via intermolecular forces (e.g., van der Waals, hydrophobic and electrostatic interactions); Irreversible adhesion via conformational changes and denaturation of proteins</td>
<td>Protein molecules change their conformations more on hydrophobic surfaces than on hydrophilic surfaces</td>
</tr>
<tr>
<td></td>
<td>Diatoms</td>
<td>Temporary attachment via extracellular polymeric substances; Permanent attachment via pads, stalks, tubes, or films</td>
<td>Diverse and abundant group of unicellular protists and the major component of microbial slimes</td>
</tr>
<tr>
<td>Macrofouling</td>
<td>Bryozoa</td>
<td>Depending on larva age, species present and bacterial density on the surface: Temporary attachment via acid mucopolysaccharide adhesive; Permanent attachment via a combination of proteins and acid mucopolysaccharides</td>
<td>One of the most common macroorganisms in marine biofouling</td>
</tr>
<tr>
<td></td>
<td>Barnacles</td>
<td>Temporary attachment via cyprid cement containing crosslinked o-quinones; Permanent attachment via adult cement (three groups of proteins that contain high levels of amino acids serine, threonine, glycine, and alanine)</td>
<td>Attach to almost all surfaces underwater, normally spending all their life in the same place</td>
</tr>
<tr>
<td></td>
<td>Mussels</td>
<td>Temporary attachment via glycoproteins; Permanent attachment via cross-linked scleroproteins</td>
<td>Permanent adhesive is very strong and durable</td>
</tr>
<tr>
<td></td>
<td>Algae</td>
<td>Initial attachment via the flagella of motile spores and extracellular residual muclage present on the spore surface; Permanent attachment via secreted adhesive material discharged through the plasma membrane in the region of substratum-surface contact</td>
<td>Permanent adhesives of green, brown, and red algal spores are glycoproteins (i.e., polysaccharide-protein complexes)</td>
</tr>
</tbody>
</table>

**Fig. 4.** Various coating properties that can be manipulated to control the organisms’ interaction with the surface. While the antifouling performance is governed by physicochemical interactions, the compatibility with cleaning depends on mechanical properties. The fouling-release performance can be manipulated by both types of interactions and offers a vast potential for a targeted coating design.
In general, depending on the surface properties, biofouling control can be realized by three fundamental approaches:

(i) Prohibiting contact or killing of attached organisms by antifouling coatings,
(ii) Hindering permanent settlement by fouling-release coatings,
(iii) Removing the strongly attached biofouling by cleaning.

3.1. Surface free energy

The free energy of a surface is the basic property that governs the physicochemical interaction with approaching bioorganisms when submerged in seawater.

General definition: It is a measure of the energy which is necessary to break chemical bonds in order to create a new surface from bulk solid or liquid. Since energy is always needed to break bonds, surface free energy represents the excess energy possessed by the surface compared to the bulk of the material. There is the tendency for a surface to minimize its area, as the system is only thermodynamically stable when its free energy is minimized. Therefore, surfaces with high surface free energy are easily covered by materials with low surface free energy. Materials with strong bonds typically have high surface free energy. For solid surfaces, the concept of surface free energy can be applied in vacuum systems. However, liquids cannot be treated in a vacuum, thus, as a realistic concept, interface energy is a more important quantity. The interface energy is defined as the energy to enlarge an interface, which strongly depends on the interaction and intermolecular forces between the surfaces. Strong attractive forces generate strong interactions and result in low interface energies.

Influence on the biofouling formation: Surface free energy is one of the most important physicochemical properties of solid surfaces, which influences the formation of fouling on solid surfaces. The relationship between surface free energy and relative bio-adhesion has been illustrated in the Baier curve (Fig. 5), based on which marine antifouling and fouling-release coatings can be designed [88]. Fouling-release coatings with a low surface free energy of about 22–24 mN/m can reduce interactions between the organism and the substrate and thus exhibit minimum bio-adhesion. As a result, attached organisms are easily removed when sufficient shear forces are present [85]. In contrast, antifouling coatings with high surface energy similar to water (72 mN/m) provide good resistance to fouling attachment due to the formed hydration layer. Since the interface energy between the surface and water is minimized, it is energetically beneficial for the surface to maintain contact with water rather than with marine organisms [89].

3.2. Surface topography

Surface topography plays a significant role in the way marine foulers interact with, settle on, and adhere to a surface [89]. Essentially, it can influence the biofilm adhesion in a twofold way.

(i) According to the surface wettability: Especially in the nanoregime, the topography can have a strong influence on the wettability of the surface [90]. Mediated by the aspect ratio and spacing of the topographic features, it can promote either fouling-release or antifouling properties of a surface. This aspect will be explained in Section 3.3.

(ii) According to the available contact area: The surface topography has a direct influence on the contact area available for different types of organisms (Fig. 6) and thus can have a purely area-related effect on the organisms’ adhesion. Generally speaking, the more area is available the more settlement will take place and the more area is covered per organism the higher the force necessary to remove it.

Area-related influence on the biofouling formation: The available contact area is influenced by the size, spacing, aspect ratio, and (micro-)roughness of the topographic features [53,91,92]. Fig. 6 exemplarily illustrates in which way the attachment situation can be correlated with these properties. Since the different biofouling organisms have very different sizes (bacteria ≤ 1 μm; spores ca. 5–7 μm; larvae ca. 120–500 μm), there is no universal topographical effect on the adhesion area of a biofouling film. Instead, its influence expresses itself differently for each organism. Nevertheless, several empirical models, such as the attachment point theory, the engineered roughness index model, and the surface energetic attachment model, have been proposed to generalize and illustrate settlement mechanisms of fouling organisms on surfaces.
with specific topographic features [54]. For instance, proposed by Scardino et al. [93], the attachment point theory suggested that more attachment points during settlement resulted in a higher and stronger attachment. Here, the lowest degree of the settlement was obtained on microstructured surfaces with the feature spacing being slightly smaller than the size of fouling organisms, as there were minimum attachment points available.

3.3. Surface wettability

**General definition:** As a measure of the wettability of a surface, the contact angle is used. The contact angle is defined as the angle at which the liquid/gas interface meets the solid surface (Fig. 7a) [94]. On an ideal solid surface that is atomically smooth and chemically homogeneous, the contact angle represents the equilibrium state established in the interplay between the solid-liquid, solid-gas, and gas-liquid interface energies (γSL, γSG, and γLG, respectively) [95]. Described by Young’s Eq. (1) [95], the value of the contact angle (θ) can be calculated by

\[
\cos \theta = \frac{\gamma_{SL} - \gamma_{SG}}{\gamma_{LG}}
\]  

A completely wetted surface with a contact angle of 0° is denoted as superhydrophilic (Fig. 7c) [96]. Surfaces with contact angle up to 90° are defined as hydrophilic (Fig. 7a), while a hydrophobic surface exhibits a contact angle above 90° (Fig. 7b). Contact angles above 120° can only be achieved on rough surfaces. When water contact angles reach values larger than 150°, such surfaces are called superhydrophobic (Fig. 7d) [96].

**Influence of the topography on wettability:** For a rough surface, Young’s equation does not apply anymore. When the wetting is homogeneous on a rough surface (Fig. 7e), the contact angle is calculated by the Wenzel Eq. (2) [97]. Whereas the heterogeneous wetting, i.e. with cavities below the droplet (Fig. 7d), is described by the Cassie-Baxter state Eq. (3) [98]. The roughness factor r is defined as the rough surface area A_rough divided by the projected flat surface area A_{flat} and f is defined as the wetted fraction of the solid surface.

\[
\cos \theta_W = \frac{\gamma_{SL} - \gamma_{SG}}{r \gamma_{LG}}
\]  

\[
\cos \theta_B = \frac{\gamma_{SL} - \gamma_{SG}}{f \gamma_{LG}} + f - 1
\]  

**Contact angle hysteresis:** Although contact angles are commonly used to describe surface wettability, contact angle alone is inadequate to evaluate the hydrophobicity of a coating [99,100]. The force (F) needed for a drop to move over a solid surface is determined by \( F = \gamma_{LG} (\cos \theta_W - \cos \theta_A) \), where \( \gamma_{LG} \) is the surface tension of the liquid, and \( \theta_W \) and \( \theta_A \) are the receding and advancing contact angle of the liquid on the solid surface, respectively [101]. The difference \( \theta_W - \theta_A \) is defined as the contact angle hysteresis, which governs the roll-off angle of a liquid droplet on a solid surface (Fig. 7e) [101,102]. It arises from the topographical or chemical surface defects which pin the contact line [103]. If there were no hysteresis, a drop would slide or roll-off at the slightest tilt of the surface. Contact angle hysteresis is a direct indication of the resistance to liquid or adhesive penetration and surface reconstruction [104].

**Influence on the biofouling formation:** The wettability of a coating by water has a major impact on the anti fouling/fouling-release performance of the coating. In the development of biofouling control coatings, low surface energy materials such as PDMS and fluoro polymers are commonly used to fabricate the (super-) hydrophobic surfaces. By incorporation of micro-/nanoparticles or lubricants, superhydrophobic surfaces with low contact angle hysteresis can be achieved, which is related to good fouling-release performance. In contrast, poly(ethylene glycol) (PEG), acrylate-based, and zwitterionic polymers are commonly used for preparing (super-) hydrophobic coatings, where the formed hydration layer acts as a barrier to resist the attachment of proteins and marine organisms (Section 4).

3.4. Elastic modulus and thickness

The elastic modulus, as well as the thickness of a coating, can also have a decisive impact on the biofouling control performance. Which impact these properties have depends on the type of coating:

(i) In the case of fouling-release coatings, elasticity and thickness can be exploited to manipulate the preferred failure mechanism at the joint between the surface and the bioorganisms (Fig. 8a-c) [32,105].

(ii) For antifouling coatings, however, it is the thickness that plays a role in terms of their long-term performance (Fig. 8d and e).

3.4.1. For fouling-release coatings

The critical stress \( \sigma_c \) and the critical force \( P_c \) to remove a disk from the coating (Fig. 8a) is:

\[
\sigma_c = \sqrt{\frac{2G_LK}{t}}
\]  

\[
P_c = \pi a^2 \sqrt{\frac{2G_LK}{t}}
\]  

where \( G_L, K, t, \) and \( a \) are the critical surface energy, bulk modulus, thickness of the film, and contact radius, respectively. This means that optimum fouling-release coatings should not only have low surface energy, but should also be mechanically soft and (up to a certain point) rather thickly applied. By adjusting the surface free energy, elastic modulus, and thickness of a coating, different release mechanisms can be achieved [32,105]. This can be illustrated...
by a closer look at two prominent examples: fluoropolymers and silicone elastomers.

For fluoropolymers: Fluoropolymers with a glass transition temperature above room temperature have a relatively high elastic modulus (value range in GPa) which is unfavorable according to Eq. (4) and (5). Nonetheless, fouling-release can take place since they have a relatively smooth and low energy surface [106]. Additionally, due to the high resistance of their surface to interdiffusion and rearrangement of molecules, the joint can be easily fractured in shear (Fig. 8b).

For silicone elastomers: The situation is different for silicone elastomers. When subjected to a normal force, the silicone is sufficiently soft to have appreciable deformation, where the organism peels off easily (Fig. 8c). However, this also requires a thick coating layer.

Silicones have higher surface energy than fluoropolymers, resulting in a stronger bond with attached organisms. However, the bulk modulus of fluoropolymers is much higher than that of silicone elastomers. Thus, the joint failure at the silicones/organism interface occurs in peeling, requiring less energy, while the joint on fluoropolymers fails at higher critical stress in shear [32,105].

3.4.2. For antifouling coatings

Generally, sufficient antifouling and long-term performance of a coating can be influenced by:

(i) The stability of hydration layer formed on the (super-)hydrophilic surfaces,
(ii) The self-polishing or degrading rate of the outer layer of the coating (Section 5),
(iii) The type and release rate of the antifouling agents from the coating (Section 6).

Since all these aspects are related to the thickness of the coating, the thickness must be taken into account not only for the fouling-release performance but also for the antifouling performance.

For (super-) hydrophilic coatings: For (super-) hydrophilic coatings based on polymer brushes, the surface hydration might be insufficient if the polymer film is too thin, which leads to worse antifouling properties. However, a polymer film that is too thick might lead to reduced antifouling performance due to self-condensing of the long polymer chains (causing weaker polymer-water interactions) [107]. For example, the optimum film thickness of poly(HEMA-co-PEG10MA) copolymer brushes ranges from 200 to 400 Å in terms of their resistance to the attachment of protein, marine bacterium Cobetia marina, and zoospores of the marine alga Ulva linza [108].

For self-polishing coatings and coatings containing antifouling agents: In the case of self-polishing coatings and coatings containing antifouling agents (Fig. 8d and e), the surface is eroded and renewed regularly, or the antifouling agent is released continuously from the coating matrix. Thus, the thickness of the coatings influences the service lifetime of the coatings [109].

3.5. Chemically active components

The biofouling control property of a coating can be achieved by the incorporation of chemically active components, such as:

(i) Natural and synthetic antifouling agents,
(ii) Self-renewable polymers,
(iii) Stimuli-induced switchable components.

Incorporation of antifouling agents: Antifouling agents can prevent the attachment of marine organisms by inhibiting their biological activities. For example, indole derivatives as alternative biofriendly antifouling agents can trigger algal cellular Ca\(^{2+}\) efflux, thus interrupting the Ca\(^{2+}\) balance of cells and the growth of organisms (Section 6) [110]. The active antifouling agents can be either isolated from living organisms or synthesized chemically [111–113]. Several characteristic values are commonly used in literature to quantify the suitability of substances as future antifouling agents. The EC\(_{50}\) value is defined as an effective concentration.
of the antifouling agent inducing a 50% inhibition of biological activities of the test organisms. The LC$_{50}$ stands for the lethal concentration, i.e., the concentration required to kill 50% of the test organisms. A compound with an EC$_{50}$ value < 25 µg/mL and an LC$_{50}$/EC$_{50}$ ratio > 15 is usually considered as a nontoxic antifouling agent [114]. However, Qian et al. reported that when selecting candidates for antifouling agents, only compounds with EC$_{50}$ value < 5 µg/mL and an LC$_{50}$/EC$_{50}$ ratio > 50 should be considered for future development from an environmental point of view. In addition, compound solubility and stability are the other two essential parameters that should be taken into account when developing new antifouling agents. For example, a compound with a low therapeutic ratio may still be considered if it degrades easily in the marine environment due to reduced wide range negative effects on non-target organisms and therefore the ecosystem [115,116].

Self-renewable coatings: As for the self-renewable coatings, the chains of these polymers can be hydrolyzed by ions (e.g., Na+, Cl—, etc.) in seawater and undergo biological degradation to achieve surface self-renewal performance [117]. The antifouling performance of such coatings is related to the polishing and degradation rate of the coatings (Section 5). For example, the degradation process of degradable polymers can be summarized into two steps: (i) The preferential degradation of amorphous polymer fractions occurs at the initial stage; (ii) Subsequently, the slower-degrading crystalline parts start to degrade [118]. Therefore, the high crystallinity of polymers retards the degradation process, and the degradation can be regulated by adjusting the crystallinity.

Switchable polymers: Switchable polymers exhibit reversible phase transition in response to changes in the surrounding environment (e.g., pH, temperature, and light, etc.), resulting in surfaces that are unfavorable for organisms to attach or surfaces on which the attached organisms can be easily released (Section 7).

4. Coatings based on surface wettability

Surface wettability is strongly influenced by surface free energy and topography (Section 3.3). It is one of the most important surface parameters involved in the development of new marine coatings for biofouling control [119] and can be exploited to achieve fouling-release as well as antifouling properties. Here, the three most important surface types are (super-) hydrophobic, (super-) hydrophilic, and amphiphilic. This section will discuss recently developed fabrication processes as well as the performance of such modern surface coatings.

4.1. (Super-) hydrophobic coatings

Hydrophobic surfaces exhibit a non-wetting behavior and are defined as surfaces with a water contact angle higher than 90°, while surfaces with a contact angle larger than 150° are termed superhydrophobic (Section 3.3) [120]. (Super-)hydrophobic surfaces have been applied in various fields, where their self-cleaning [121–123], antifogging [124,125], and biofouling control [126,127] properties have been used. In recent years, there has been an increased interest in fabricating (super-) hydrophobic coatings with fouling-release properties to control biofouling in the marine sector [128–130]. Due to the lack of strong polar interactions, (super-) hydrophobic surfaces reveal low surface energy and exhibit only weak dispersive interactions with biomolecules, which makes the removal of the attached biofouling easier [89]. However, the low surface energy of material often leads to low adhesion-to-substrate strength [131]. There are four types of polymer coatings, which will be discussed in the following. They all possess surfaces that exploit slightly different fouling-release approaches:

(i) Polymethylsiloxanes (PDMS) are extraordinarily soft with low surface energy and especially promote an easy fouling-release in a peeling-off process [32].
(ii) Fluoropolymers have a relatively smooth and low energy surface, and bioorganisms can only adhere very weakly [106].
(iii) Slippery coatings are hydrophobic and lubricated by oil, which hinders the attachment of different bioorganisms [132].
(iv) Superhydrophobic coatings possess self-cleaning property through the synergic effect of low surface energy and nano/microroughness of the surface [133].

4.1.1. PDMS-based coatings

PDMS is a well-known hydrophobic material that belongs to the class of elastomers and has a low surface free energy as well as a low elastic modulus required for a successful fouling-release performance [134]. However, these properties also cause PDMS coatings to exhibit poor adhesion to substrates and low resistance to mechanical damage, limiting their application in the marine sector [131,135]. Therefore, extensive research has been carried out on modifications of pure PDMS by the fabrication of PDMS-based copolymers, composites, and the incorporation of additives. As illustrated in Fig. 9, the development of PDMS-based coatings focuses on the improvement of mechanical stability, substrate adhesion strength [136,137], as well as the optimization of surface properties to achieve the most efficient biofouling control performance for long-term marine applications [138–142]. For ship coatings, the fouling-release performance of pure PDMS coatings is influenced by the vessel's speed, the time spent in port (resting), as well as the extent of biofouling and the life stage of the attached organisms, which leaves significant room for improvements of the surface properties [143].

The following examples illustrate the various optimization routes, as indicated in Fig. 9, which can be followed when designing PDMS-based coatings:

4.1.1.1. Improvements of the fouling control performance. For example, Martinelli et al. [144] tested the effect of different surface-active side-chains on the fouling performance of a PDMS-based copolymer. They synthesized block copolymers from PDMS and poly(methyl)acrylate with oxyethylene or fluoroalkyl side chains as surface-active components (Fig. 10a), which were then incorporated into a PDMS matrix. The PDMS-based composite containing oxyethylene chains showed better fouling-release performance against sporelings (young plants) of U. linza and juveniles of Balanus amphitrite than pure PDMS, while no settlement of B. amphitrite cyprids was detected on fluoroalkyl chain-contained PDMS.

Sun et al. [148] manipulated the surface hydrophobicity via topographical modifications. They mechanically mixed carbon nanotubes into the PDMS matrix, by which the hydrophobicity of PDMS was improved. A lower degree of biofouling was found on the carbon nanotube-modified PDMS. This was attributed to the topographical changes and accordingly increased hydrophobicity, which affected the colonization and successional dynamics of pioneer biofilm communities, particularly the early eukaryotic communities.

Lu et al. [145] introduced natural biocide containing nanospheres into a PDMS-based copolymer and applied a mechanically supportive layer underneath. They used the natural product antifoulant capsaicin (a chili pepper’s component), bounded it to CoFe$_2$O$_4$/gelatin magnetic nanoparticles, and then mixed the resulting nanospheres (FeCap) with a PDMS-based block copolymer polystyrene-block-poly(dimethylsiloxane-stat-vinylmethyilsiloxane) (PSDV) (Fig. 10b). To control the elastic modulus of the PSDV/FeCap, a layer of polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) was introduced underneath. Compared to a smooth glass surface as
well as pure PSDV and SEBS layers, the PSDV/FeCap active layer exhibited the lowest settlement of Navicula subminusscula due to its oriented nano-rough topography and nonleaking capsacin on the surface. Also, Peres et al. [149] investigated the effect of a natural antifouulant. They modified PDMS by adding propolis powder (originating from bees), known for its antimicrobial and bactericidal activity. As shown in an 11-month field experiment, the incorporation of propolis decreased the degree of biofouling and acted as an anti-corrosion additive. Other than in the latter two examples, Tian et al. [150] used an inorganic antifouulant and incorporated antibacterial silver nanoparticles into their coating. They synthesized a new hybrid PDMS-based coating with nanocomposite hydrogel and silver nanoparticles (AgNPs). The incorporation of AgNPs improved the interfacial compatibility between the hydrophilic hydrogel and hydrophobic PDMS by acting as a crosslinker, whereby the hydrophilic hydrogel was well dispersed in the PDMS matrix. The prepared hybrid coatings showed good antibacterial performance against Escherichia coli as well as anti-algae performance. After two years of sea immersion, less biofouling and no barnacles were found on the surfaces of the hybrid coatings in contrast to pure PDMS coating and bare substrate. The coatings containing natural and synthetic antifouling agents will be discussed in detail in Section 6.

4.1.1.2. Mechanical stability and adhesion to the substrate. Improvement of the long-term mechanical stability and adhesion to the substrate of PDMS is another challenging task, since it should not compromise the fouling-release surface properties of PDMS. The following examples show how copolymerization and intermixing micro-nanoparticles can be used to achieve this goal:

For example, Liu et al. [131] synthesized PDMS-based polyurea (PDMS-PUa) via a polycondensation reaction (Fig. 10c). The PDMS-PUa inherited not only low surface energy and hydrophobicity from the nature of PDMS, which ensured good fouling-release performance of the coating on dynamic conditions, but also high adhesion to the substrate from polyurea. The improved substrate adhesion of PDMS-PUa is attributed to the phase separation between the 1,6-hexanediane hard segments and PDMS soft segments (Fig. 10d), where the urea groups in the PDMS-PUa can form hydrogen bonds with active groups on a substrate surface. To prevent microorganisms from settling on the PDMS-PUa coating under static conditions, Liu et al. [151] mixed a small amount of organic antifoulant (4,5-dichloro-2-n-octyl-4-isothiazolin-3-one) (DCOIT) into the PDMS-PUa coating. Although DCOIT is prone to stay in the polymer matrix due to the hydrophobic long alkyl chain in DCOIT, the low solubility of DCOIT in seawater, and chemical affinity of the electron-rich oxygen and nitrogen atoms in DCOIT to urea groups, DCOIT would migrate to the surface driven by osmotic pressure and gradually dissolve into the seawater. The release rate of the biocide DCOIT was regulated by its concentration, which determined the long-term effectiveness of its biofouling control properties. Zhang et al. [137] proposed another copolymer system. They fabricated a PDMS-modified polyurethane (PU) copolymer structure, which exhibited lower surface free energy than pure PU. The presence of PDMS promoted the removal of weakly attached organisms on the surface. However, the highest mechanical tensile strength of the copolymer has reached only 2.09 MPa.

To overcome the poor mechanical properties of PDMS that are insufficient for most marine applications, Qiu et al. [136,146] developed PDMS-polythiourethane (PTU) composites reinforced with tetrapodal shaped micro-nano ZnO particles. PTU is a hydrophilic, UV-stable, and biocorrosion-resistant polymer that is mechanically well-suited as a matrix polymer to form a composite for maritime applications (Fig. 10e) [39]. Due to phase separation between PDMS and PTU during the polymerization process, micro-sized PDMS domains on the surface of the composite were formed (Fig. 10f), and therefore the hydrophobic properties of PDMS were transferred to the mechanical stable polymer matrix. The hard biofouling adhering to the composite coating surface could be easily removed without leaving any calcified residues, similar to pure PDMS, and in contrast to the reference materials AlMg3 and polyvinyl chloride (PVC) (Fig. 10f and 10g).

4.1.2. Fluoropolymer-based coatings

Besides PDMS, fluoropolymers are the other essential material family used for the fabrication of hydrophobic fouling-release coatings [152]. Due to the smooth and low-energy surface of fluoropolymers, only weak interface bonds form between the marine organisms and the coating [17]. However, fluoropolymers have several drawbacks compared to PDMS-based coatings:

(i) The fouling-release requires a relatively high critical stress or shear force: In contrast to PDMS surfaces, from which the attached organisms are removed by a peeling fracture mechanism, the high resistance of fluoropolymers to molecular inter-diffusion and rearrangement leads to a sharp and well-defined interface, which ruptures by shear [17,152]. As the bulk elastic modulus of fluoropolymer is higher than that of the PDMS elastomers, the joint fails under higher critical stress (Section 3.4) [17].

(ii) Fluorinated pollutants may harm the environment: The ubiquitous presence of fluorinated organic compounds in environmental media raises public interest and questions about the safety of
Fig. 10. Examples of (super-) hydrophobic biofouling control coatings. PDMS-based coatings with improved fouling control performance: a) block copolymers made from PDMS and poly(meth)acrylate with oxyethylene or fluoroalkyl side chains [144]. b) Preparation of antifouling coating with oriented nano-topography and nonleaking capsaicin [145]. Copyright 2018. Adapted with permission from American Chemical Society. Mechanical reinforcement of PDMS-based coatings: c) Synthesis of PDMS-based polyurea (PDMS-PUa) via a polycondensation reaction. d) Illustration of the improved substrate adhesion of the PDMS-PUa coating while maintaining good fouling-release properties [131]. Copyright 2016. Adapted with permission from American Chemical Society. e) Synthesis of polythiourethane (PTU) by polyaddition reaction [39]. f) Energy-dispersive X-ray analysis of PTU/PDMS composite before sea immersion and after 12 months of sea immersion and mechanical cleaning. The Si, C, Ca signals refer to PDMS, PTU, and barnacle residues, respectively [146]. Copyright 2021. Adapted with permission from American Chemical Society. g) Comparison of test surfaces, before and after barnacle removal [136]. Fluoropolymer-based coatings: h) Synthesis of fluoropolymers [147].
PTFE (and perfluorooctanoate) and other fluoropolymers that rely on perfluorooctanoate in their synthesis. These compounds have been detected in marine biota and even in human sera. Due to their unique chemical and biological stability, they can preclude any degradation or metabolism, resulting in bioaccumulation and persistence [153–155].

(iii) The chemical stability of the surface in seawater is low: A fatal drawback of fluoropolymers is that they often undergo rapid chain reorganization in water, leading to a loss of their hydrophobicity and fouling-release properties [147]. To improve the long-term stability of fluoropolymers, the fluorinated side chains of the polymer should be capable of organizing into an ordered structure on the surface while maintaining a high density of –CF3 groups on the coating surface [147,156]. Another approach is to limit the chain mobility of the polymer through the chemical crosslinking of groups, such as epoxy-functional groups [157]. For example, Zhu et al. [147] designed and synthesized functional crosslinkable fluoropolymers. They are composed of short fluoroalkyl groups or perfluoropolyether substituted fluorinated styrene, methyl methacrylate, and glycidyl methacrylate through a free radical polymerization (Fig. 10H).

4.1.3. Slippery coatings

Slippery surfaces, commonly known as SLIPS (slippery liquid-infused porous surfaces), are surfaces that exhibit a low contact angle hysteresis (Section 3.3). While static measurements of contact angles give an initial insight into surface wettability, information on the surface's chemical and topographical heterogeneity and its sliding properties can be gained from dynamic contact angle measurements by defining a so-called contact angle hysteresis. It was shown that to achieve a good fouling-release performance, both a large water contact angle and a low contact angle hysteresis are required [104].

A common approach to reduce contact angle hysteresis and achieve slippery surfaces is to mix oily lubricants into hydrophobic coatings [158,159]. The following examples illustrate that researchers recently tested the effect of slippery coatings on different bioorganisms using different composite systems and lubrication approaches:

For example, Ba et al. [160] tested the response of diatoms to a PDMS surface lubricated by silicone oil. They incorporated methylphenyl silicone oil with different viscosities into PDMS by stirring. PDMS coatings modified with high viscosity silicone oil exhibited the lowest adhesion and highest removal rate of benthic diatoms. The performance improvement was attributed to increased hydrophobicity, decreased elastic modulus, and prolonged time of silicone oil leaching. Amini et al. [161] basically used the same material system and investigated the response of mussels to such a surface. They demonstrated in laboratory and field studies that silicone oil-infused PDMS coatings significantly reduce mussels’ attachment. It has been suggested that lubricant infusion deceives mussels’ mechanosensing ability, inhibits adhesive threads’ secretion, and decreases the molecular work of adhesion, leading to low attachment frequency and much lower attachment strength.

Other as in the studies presented above, and due to the poor mechanical durability of PDMS, Galhenage et al. [162] used a siloxane-PU (SiPU) system for the incorporation of silicone oil. The resulting coating displayed improved fouling-release performance while providing good mechanical and adhesion-to-substrate properties. Zhang et al. [163] fabricated a self-healing slippery organogel and investigated the bacterial attachment. This was done by infusing silicone oil into a PDMS-based polyurea (PDMS-PUa) matrix. The organogel exhibited low water sliding angle of < 10° and excellent performance in inhibiting bacterial (Pseudomonas sp.) attachment. After cutting the material into two pieces and putting them back in contact, a complete self-healing, i.e., acquisition of original tensile test and sliding angle values, was obtained after 48 h at room temperature or 24 h at 60°C.

Following a biomimetic approach, Ware et al. [164] mimicked the lubricating mechanism of the pitcher plant. This was done by fabricating nanostructured wrinkled surfaces from Teflon, polystyrene, and poly(4-vinylpyridine) and infusing silicone oil into the wrinkles. Infused surfaces inhibited the growth of Pseudomonas spp. bacteria up to 99% and mitigated the attachment of algae in the 7-week field test. However, the algal attachment increased as the silicone oil slowly depleted over time.

4.1.4. Superhydrophobic coatings

On superhydrophobic surfaces, the water contact angle exceeds 150°. As a result, the water forms spherical droplets and rolls over the surface, carrying away contamination [165,166]. This self-cleaning phenomenon is known as the lotus effect, and it originates from the low surface energy combined with the nano/microroughness of the surface [167] (Section 3.3). However, for the design of long-term stable superhydrophobic coatings for marine applications, not only physicochemical properties of the surface, but also mechanical interactions governed by the coating thickness, mechanical stability, and adhesion to the ship hull are essential and were addressed by several authors [120,168,169]. The following examples give insight into the different surface structuring methods investigated in recent years, especially by using the various nanoparticles and polymer matrix systems as well as biomimetic approaches:

PDMS-based coatings: Selim et al. developed superhydrophobic PDMS-based coatings with improved biofouling control properties by incorporation of various nanoparticles [133,141,142,170–174]. For example, in [141], it was shown that the addition of 0.1 wt% spherical Ag nanoparticles significantly improved the surface hydrophobicity, inertness, fouling resistance, and easy-to-clean properties without affecting the bulk mechanical properties. Furthermore, vinyl-terminated PDMS/β–Al2O3 nanorod composites with lotus-like nanostructure were fabricated, whereby coatings with 0.5 wt% nanofiller possessed the highest water contact angle, lowest surface free energy, and highest cell growth inhibition [142]. In further studies, a similar effect of improving surface hydrophobicity and fouling prevention performance was observed when incorporating nano-magnetite particles [170], ZnO nanorods [133], β–MnO2 nanorods [172], silicon carbide nanowires [173], nanorod-like TiO2–SiO2 particles [174], or graphene oxide anchored with alumina nanorods [171] into the PDMS matrix.

Other polymer systems: Several superhydrophobic surfaces were produced from materials other than PDMS. For example, López-Ortega et al. [175] achieved superhydrophobic surfaces by incorporating SiO2 nanoparticles into commercially available epoxy paint, and improved bactericidal activity of the coating by adding Cu3O nanoparticles. Brown et al. [176] used the solvent phase-separation method to synthesize superhydrophobic PVC surfaces, which showed promising results in a biofilm adsortion test under laboratory conditions.

Biomimetic coatings: Often, the design of superhydrophobic surfaces is inspired by structures and materials found in nature. For example, Gangadoo et al. [177] fabricated a superhydrophobic surface by replicating the surface topography of cicada and dragonfly wings with epoxy resin. Replicated surfaces demonstrated a reduced level of protein adsorption as well as limited slime and mass adsorption in a 7-day biofouling assay, indicating potential in resisting early-stage biofouling. In another exemplary work, Qin et al. [178] developed a dual bio-inspired shark-skin and lotus structure for fabrication on commercial PU polymers. Mesoporous silica nanospheres were then sprayed on the shark-skin-patterned PU surface to produce hierarchical micro- and nanostructures. As a result, a contact angle of 147° was obtained, and contact angle
hysteresis was decreased by 20% compared to the nontreated surface. Further details about biomimetic coatings will be described in Section 8.

In summary, the main hydrophobic fouling-release coatings are based on PDMS and fluoropolymers. PDMS-based coatings are commercially available. However, these coatings lack biofouling control properties under static conditions, since a certain shear force (e.g., present when the ship is moving at a certain speed) is required to achieve an optimal fouling release performance. This is why several approaches have been developed recently to improve the static fouling-release performance:

(i) Incorporation of antifouling agents,
(ii) Fabrication of superhydrophobic surfaces by introducing micro-/nano rough structures (e.g., with micro-/nanoparticles),
(iii) Increase the surface slippage by the addition of oily lubricant.

Furthermore, research focuses on the improvement of the mechanical and adhesion-to-substrate properties of PDMS-based coatings without downgrading their fouling-release performance. This can be achieved through the synthesis of the copolymer or the blending with a stable polymer matrix (e.g., PTU).

Compared to PDMS coatings, fluoropolymers have an even lower surface free energy and also show surface hydrophobicity. However, due to their high elastic modulus, they require higher shear force to release the biofouling organisms than PDMS coatings (Section 3.4). Additionally, due to high prime costs and difficulty in processing (immiscibility in common organic solvents), there are currently few commercial products based on fluoropolymers [179,180].

4.2. (Super-)hydrophilic coatings

Hydrophilic surfaces have a strong affinity to water and exhibit water contact angles below 90° [181]. As discussed in Section 3.3, the high wettability of such surfaces results from surface chemistry, i.e., high surface free energy and surface morphology. By a proper combination of surface chemistry and roughness features, superhydrophilic surfaces with a water contact angle lower than 10° can be achieved [169,182]. (Super-) hydrophilic materials have been extensively investigated as antifouling coatings for a wide range of applications in biomedical engineering and the marine industry [183–186]. As illustrated in Fig. 11, the antifouling properties of these materials are attributed to the strong surface hydration layer, which acts as a physical and energy barrier for the organism’s settlement. Biological molecules such as proteins, as well as bacteria and other marine organisms, are unable to displace tightly bound surface water molecules, preventing them from adhering to the surface [187,188]. For example, it was shown that mussels do not settle on these surfaces due to the strong surface hydration, even after forcing the adhesion of the animals by holding them in place on the surface with rubber bands [187]. Hydrophilic polymers that proved effective to resist the attachment of marine organisms mainly include poly(ethylene glycol)-based, acrylate-based and zwitterionic polymers [189–191], which can be fabricated as hydrogels or surface-grafted brushes:

(i) Hydrogels: 3D crosslinked networks of hydrophilic polymer chains that contain water. They are distinguished from solid materials by the abundant composition of water (60–99 wt%) and low elasticity (elastic modulus 100–10,000 times lower than that of common solids) [192,193]. Due to the strong hydration ability and low elastic modulus, hydrogels can inhibit marine organisms’ attachment (e.g., germination of spores and settlement of barnacles) [194].

(ii) Polymer brushes: macromolecular structures with polymer chains densely tethered to another polymer chain or a solid sur-

face [195]. Polymer brushes can inhibit biofouling and biocorrosion by incorporating functional groups with anti-adhesion, antimicrobial, and anti-corrosion properties. Tethering polymer brushes to material surfaces can be accomplished either by “grafting-to” (via physisorption or covalent bonding) or “grafting-from” (surface-initiated polymerization) approaches [193].

4.2.1. PEG-based coatings

Among the recently developed (super-) hydrophilic coatings, PEG is one of the most successful hydrophilic polymers that has been applied in biomedical and marine environments [186,197]. The antifouling properties of PEG are mainly attributed to (i) the low PEG–water interfacial energy, (ii) the hydration layer forming due to the hydrogen bonding between the water molecules and the ether oxygen atoms, and (iii) the mobility and flexibility of the PEG chains [198,199]. Moreover, due to the electrical neutrality of PEG, the electrostatic interactions with charged protein domains can be reduced [200,201]. Long-chained PEG can also prevent protein adsorption by steric hindrance [193,202,203].

4.2.1.1. Hydrogels. Several attempts have been made to produce PEG-based hydrogel coatings [204–207]. For example, Ekblad et al. [207] fabricated a thin PEG-based hydrogel coating by UV-initiated free radical polymerization and showed a limited settlement behavior of a diverse group of marine and freshwater organisms in laboratory tests. Although, in general, hydrogel-based coatings demonstrate considerable antifouling performance, they, in reality, suffer from the fatal weaknesses of short-term stability since they can be easily damaged due to their poor mechanical properties and poor adhesion to substrates [194]. Moreover, due to their high hydrophilicity, hydrogels strongly absorb water and can be easily damaged underwater [208]. Thus, for long-term applicability, there is an urgent need to improve the mechanical properties of hydrogel-based coatings.

4.2.1.2. Polymer brushes. PEG brushes have received broad attention for the fabrication of antifouling coatings due to their non-leaching and thus environment-safe mechanisms [193]. Further-
more, using a grafting approach allows to circumvent the adhesion and stability issues of hydrogel-based hydrophilic coatings. A well-adhering and mechanically robust bulk polymer can thereby be equipped with an antifouling surface.

Using “grafting to” approaches, PEG can be covalently attached to surfaces to form linear polymer brushes [209]. Through a “grafting from” approach (e.g., surface-initiated atom transfer radical polymerization), PEG methacrylates can be polymerized from surfaces and thereby form linear polymer brushes with PEG side chains [210–212]. The antifouling performance and stability of PEG brushes are influenced by the grafting density, grafting type, chain length, chemistry of the end group, and the type of PEG branching architecture [201, 213–215].

Although PEG brushes demonstrate promising antifouling properties, their long-term stability is limited due to hydrolysis and biodegradation [208, 216, 217]. One idea to increase the service-life of the coatings is to incorporate the ability of self-renewal into the surface (Section 5). For example, this could be done by using the 3D grafting approach, which was recently developed. In this process, the functional segments are grafted not only to the surface but also to the interior part of the polymer due to interdiffusion phenomena [218]. Incorporating hydrophobic chains into the surface sublayers ensures the hydrophilicity reestablish after surface damage. Following this approach, Yang et al. [208] constructed a hydrophilic polymer surface by 3D grafting poly(ethylene glycol) diacrylate (PEGDA) on a bisphenol A epoxy acrylate (BEA) sheet in a UV-curing technique which showed good antifouling performance (Fig. 12a). Despite the 3D grafting approach, this performance was lost after one month in the marine environment. In contrast, Jiménez-Pardo et al. [189] used a blending and crosslinking approach to incorporate a reservoir of hydrophilic dangling chains into a three-component polyurethane-based network (Fig. 12b). They fabricated polycarbonate-poly(ethylene glycol) methyl ether polyurethane coatings, which exhibited low protein adhesion strength and self-healing functionality after damage. Thus, they achieved constant surface hydrophilicity, which was found intact even after one year of immersion in water.

Another possibility to improve the stability of the coating might be to increase the structural complexity of the hydrophilic brushes. For example, instead of using linear and purely PEG-based brushes, Su et al. [220] proposed hierarchically structured copolymer brushes fabricated via a two-step grafting approach (Fig. 12h). In a first step, they grafted polyacrylic acid (PAA) chains, which are also hydrophilic by nature, to the surface of the coating. Subsequently, different molecular weight PEG chains were grafted to the PAA brushes, forming hierarchical and comb-like hydrophilic polymer brushes. These surfaces showed excellent hydrophilicity and antifouling properties in a field test for two months.

4.2.2. Hydroxy-functional acrylate-based coatings

Similar to PEG chains being terminated by a hydrophilic hydroxyl group, acrylate-based polymers possess inherent hydrophilicity since the acrylic group provides polarity for hydrogen bonding. To prevent potential electrostatic interactions of the surface with fouling organisms, commonly, electrically neutral acrylate-based polymers, such as poly(2-hydroxyethyl)methacrylate, poly(hydroxypropyl methacrylate), or poly(N-hydroxyethylacrylamide), are grafted onto the surface as brushes or prepared as hydrogel [211, 220, 221].

4.2.2.1. Hydrogels. In terms of acrylate-based hydrogels, Zhang et al. [190] pursued an interesting architectural approach (Fig. 12c and d): By fabricating hydrogel fibers implanted into the substrate, they achieved a coating with good substrate adhesion even in its swollen submerged state. The coating consisted of closely packed anionic hydrogel fibers with a diameter of about 100 nm each. The anionic poly(acrylic acid)-poly(sulfopropyl methacrylate) hydrogel fibers were implanted in nanoporous anodic aluminum oxide substrates. This was done in a multistep process: Pouring the precursor liquid onto the substrate, applying free radical polymerization, and finally peeling off the top layer of the hydrogel. The hydrogel fibers kept their original morphology after long-term swelling tests, indicating good stability. The surfaces showed effective fouling resistance and achieved a 90% decrease of fouling algae density in terms of Dunaliella tertiolecta and Navicula sp. compared to the substrates without hydrogel fibers.

4.2.2.2. Polymer brushes. Using acrylate-based polymer brushes, Yang et al. [219] investigated the influence of structural grafting parameters on the antifouling performance (Fig. 12e–g). 2-Hydroxyethyl methacrylate (HEMA) polymer brushes with various grafting densities and chain lengths were fabricated through surface-initiated atom transfer radical polymerization. It was shown that the settlement of microorganisms was reduced by increasing the polymer chain length and grafting density. Moreover, their results indicated that a sufficient surface hydration layer thickness played a key role in the long-term marine antifouling application.

4.2.3. Zwitterionic coatings

As discussed above, hydrophilic antifouling surfaces, such as PEG-based coatings, usually lack long-term stability and undergo degradation due to the presence of other bonds [222]. Recently, zwitterionic polymers with improved stability emerged as promising alternatives to PEG. Zwitterionic polymers are electrically neutral materials that carry an equal positive and negative charge, i.e., anion and cation groups, on the molecular chains [211, 222, 223]. Compared to the hydration of PEG and other non-ionic hydrophilic polymers via hydrogen bonding, the electrostatically induced hydration of zwitterionic polymers is more pronounced [224]. Therefore, due to the stronger hydration layer, zwitterionic polymers are expected to possess better antifouling properties [225, 226]. In addition to their excellent antifouling capacity, zwitterionic polymers are also easier and more flexible to be functionalized and designed [223].

Zwitterionic polymers can be generally divided into two types, carrying anionic and cationic groups: i) on the same monomer (e.g., phosphorylcholines and polybetaines), ii) on separate monomers, creating a mixed charge complex (e.g., polyampholytes) [194, 198]. Typical cations are quaternized ammonium, while anions are sulfonates, carboxylates, and phosphonates. Based on the type of anions, three major zwitterionic groups are sulfobetaine, carboxybetaine, and phosphorylcholine [222]. Similar to PEG-based coatings, zwitterionic polymers can be fabricated as surface-grafted brushes or hydrogels [227, 228]. In previous studies, sulfobetaine-based polymers have been the most widely synthesized and investigated due to the simplicity of the fabrication method. Carboxybetaine-based polymers have also attracted great interest since they exhibit better antifouling properties and biocompatibility compared to other zwitterionic polymers [229, 230]. As for phosphorylcholine-based polymers, their application is restricted due to the high production cost [222]. Recently, many studies have been conducted on zwitterionic coatings covering a broad range of research questions:

4.2.3.1. Structural factors. To better understand how the zwitterionic polymer structure affects the antifouling properties, Hibbs et al. [225] prepared three different structures based on polysulfone and polyacrylate (Fig. 13a). It was shown that increasing the ion content (i.e., the density of zwitterions) on the surface improved the antifouling properties.
Fig. 12. Examples of (super-) hydrophilic biofouling control coatings. a) Preparation of 3D PEGDA-grafted BEA sheets [208]. Copyright 2016. Adapted with permission from John Wiley and Sons. b) Preparation of the coating by incorporating hydrophilic dangling chains into a three-component polyurethane-based network [189]. Fabrication process of acrylate-based hydrogel fibers. d) The antifouling performance in terms of Navicula sp.: control surface anodic aluminum oxide, PAA, P(AA/SBMA0.01), P(AA/SBMA0.05), and P(AA/SBMA0.1) surfaces [190]. Copyright 2017. Adapted with permission from John Wiley and Sons. e) Preparation of acrylate-based polymer brushes with tailorable grafting density and their relevance for antifouling. f) Relative amounts of green algae attached to polymer brush decorated substrates with different chain lengths HEMA. g) Relative amounts of green algae attached on HEMA polymer brush-modified substrates with different grafting densities [219]. Copyright 2018. Adapted with permission from John Wiley and Sons. h) Preparation of hierarchical comb hydrophilic polymer brushes and their antifouling mechanism [220]. Copyright 2019. Adapted with permission from the Royal Society of Chemistry.

By keeping the density of zwitterionic groups constant, Koc et al. [231] investigated the influence of the chemical nature of the function group and the spatial arrangement of the oppositely charged moieties on their antifouling behavior (Fig. 13b). In their study, a series of sulfon- and sulfabetaine methacrylates-based polymers were prepared by using a set of systematically varied monomers where the arrangement of the ion pair in the side chain was changed from the classical linear to a novel Y-shaped geometry. It was shown that the antifouling properties of zwitterionic polymers are sensitive to the chemical nature of the functional groups. The comparison of polymers with sulfonate and sulfate groups illustrated that the polymer connection and/or spacer between the zwitterion and the polymer is also relevant. The samples containing the sulfate group showed mostly a better fouling resistance than those with sulfonate groups. Moreover, the arrangement of the charged groups in the side chains influenced the protein ad-
Fig. 13. Examples of zwitterionic biofouling control coatings. a) Structures of the synthesized zwitterionic coatings based on PSA and PU [225]. b) Structures and abbreviations of the copolymers investigated, using as main building blocks. Small amounts (1.0 mol%) of methacrylate BPEMA were incorporated as a photoreactive group to enable crosslinking of the spin-coated films [231]. Copyright 2019. Adapted with permission from the American Chemical Society. c) Examples of different polyzwitterion architectures. d) Chemical structure of the sulfobetaine monomers and the photo-reactive comonomer used [232]. e) Hydrolysis and degradation of PMTSi15 [191]. Copyright 2019. Adapted with permission from the American Chemical Society. f) Structure of ZW-DOPA [233]. Copyright 2019. Adapted with permission from the American Chemical Society.

sorption. Samples with non-linearly oriented zwitterions thereby resulted in increased protein adsorption compared to samples containing linearly oriented zwitterions.

By synthesizing and comparing two poly(sulfobetaine methacrylate)s with a different segmental orientation of the zwitterionic moiety toward the polymer backbone, Schönemann et al. [232] emphasized the importance of the zwitterionic group’s orientation on the polymer behavior and fouling resistance (Fig. 13c and 13d).

4.2.3.2. Long-term effectiveness. Although zwitterionic polymers show good resistance against the adhesion of marine organisms
(e.g., marine bacteria, algae, and diatoms), these coatings can easily lose their long-term antifouling performance once covered by inorganics [191,234]. Thus, regeneration of the polymer surface after contamination or damage is essential. Inspired by the self-renewal of silyl acrylate polymers (Section 5), Dai et al. [191] prepared a hydrolysis-induced zwitterionic monomer-tertiary carboxybetaine triisopropylsilyl ester ethyl acrylate coating, which was further copolymerized with methyl methacrylate and 2-methylene-1,3-dioxepane via radical ring-opening polymerization (Fig. 13e). The introduction of ester units into the main chain makes the polymer degradable, thereby self-renewable even under static conditions. These coatings inhibited the adhesion of marine bacteria (Pseudomonas sp.) and diatoms (Navicula incerta) and have the potential for long-term antifouling application.

4.2.3.3. Substrate adhesion. Application of zwitterionic hydrogel coatings is extremely difficult due to their poor adhesion to substrates and the strong shrinking (polyelectrolyte effect) or swelling (anti-polyelectrolyte effect) when transferred from pure water (fabrication condition) into saline solution (working condition) causing delamination. As discussed above, increasing the ion content of the zwitterionic coatings improves the antifouling properties, but at the same time, it also requires a stronger adhesive bond to the substrate to prevent enhanced coatings swelling and delamination when submerged in salty water [225]. Shen et al. [235] fabricated bicomponent zwitterionic hydrogel coatings by combining the anti-polyelectrolyte effect (swelling in seawater) of poly-N-(3-sulpropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine and the polyelectrolyte effect (shrinking in seawater) of polyacrylic acid (PAA). The coating exhibited good mechanical properties (e.g., in abrasion tests with sandy water) and weak swelling in saline solution, which could avoid peeling from the substrates while maintaining good anti-bacterial and anti-protein properties.

Regarding the practical applicability, not only the versatility and the simplicity but also the substrate-independency of the fabrication process should be considered. As shown in most of the previous studies, the coating processes can only be used for limited substrates. To design substrate-independent zwitterionic coatings, Yeon et al. [233] synthesized a zwitterionic dopamine derivative (ZW-DOPA) coating containing both catechol and amine groups by a simple one-step process (Fig. 13f). The ZW-DOPA coating could be applied on different substrates (e.g., TiO₂ substrate, stainless steel, and nylon), showing substrate-independent coating capability and high resistance to marine diatom adhesion. The oxidation of ZW-DOPA was controlled through deprotonation of catechol or the addition of an oxidant (ammonium persulfate or sodium periodate (NaIO₄)), with NaIO₄-induced ZW-DOPA being the most efficient.

In summary, (super-) hydrophilic coatings are usually fabricated in the form of graftered brushes and hydrogels. Even if critical issues such as long-term stability, good adhesion on different substrates, and productivity have been taken into account by researchers so far, there are additional factors that urgently need to be addressed in the future to promote the applicability of (super-) hydrophilic antifouling coatings in real-life:

(i) So far, antifouling studies of zwitterionic polymers were mainly conducted on proteins, bacteria, and several microorganisms such as zoospores and diatoms [228,236]. Even though they showed promising results, more research is needed under realistic maritime conditions and on macroorganisms to enable their industrial applications.

(ii) Zwitterionic polymers are usually prepared by surface-initiated atom transfer radical polymerization or layer-by-layer self-assembly, which is rather difficult to be applied on large surfaces [237–239]. Thus, new strategies in terms of the synthesis and fabrication process towards a large-scale application need to be developed.

4.3. Amphiphilic coatings

Amphiphilic surfaces have attracted attention in the last decade and are currently conceived as one more promising strategy for marine biofouling control applications [240,241]. With both hydrophobic and hydrophilic components, such surfaces can offer a broader spectrum of efficacy (Fig. 14).

As discussed in Section 4.1, purely (super-) hydrophobic coatings (e.g., PDMS-based coatings) show good fouling-release properties and allow the fouling to be easily removed by minimizing the adhesion strength between the organisms and the surface. However, hydrophobic surfaces cannot prevent the settlement of fouling organisms [35]. For example, PDMS-based coatings are unable to resist the accumulation and growth of marine slime layers composed of bacteria, diatoms, and a matrix of secreted extracellular polymeric substances [242]. Moreover, it is well known that some species, such as diatom Navicula, attach even more strongly to hydrophobic coatings (especially PDMS-based) than to hydrophilic coatings [40,243].

Likewise, purely (super-) hydrophilic surfaces (e.g., PEG-based coatings, Section 4.2) face the issues of organism’s adhesion selectivity as well. Such surfaces can prevent the settlement of the organisms at the initial state due to the formed hydration layer, but they do not readily release fouling organisms once adhered [89]. In addition, different organisms exhibit different adhesion strengths on surfaces with the same wettability. For example, the unicellular diatom Nitzchia perminuta adheres only weakly to hydrophilic surfaces, while the adhesion of macroalgae Ulva linza to hydrophilic surfaces is typically stronger [40]. Moreover, some marine organisms can even displace water from the surface interface to maximize their adhesion to diverse surfaces [244].

As illustrated in Fig. 14, amphiphilic coatings, with both hydrophobic and hydrophilic components, can therefore possess increased biofouling control efficacy. The amphiphilic polymers can provide a heterogeneous nanoscale mosaic chemical surface, where the coexistence of hydrophobic and hydrophilic domains can confuse organisms during settlement and adhesion [245]. For example, it was shown that Ulva spores were no longer able to distinguish between the fluorinated (hydrophobic) and PEGylated (hydrophilic) features on a microscale patterned amphiphilic surface where the spores regarded it as pure PEG and hence avoided settlement on the surface [246].

In general, the strategies for preparing amphiphilic coatings include (i) direct use of amphiphilic copolymers as the basic materials, (ii) incorporation of amphiphilic copolymers as surface-active additives, and (iii) grafting the amphiphilic components to the coating surfaces [247–250]. Thereby amphiphilic copolymers bearing hydrophilic (e.g., PEG) and hydrophobic (e.g., fluorinate) moieties can be synthesized through various approaches, such as sol-gel chemistry, free radical polymerization, and atom-transfer radical polymerization [251–253].

4.3.1. PDMS-based amphiphilic coatings

Numerous studies have been conducted on the modification of PDMS with amphiphilic copolymers to achieve improved antifouling and fouling-release performance. Next to their specific chemical composition, they differ in the way the copolymers were connected to the PDMS.

4.3.1.1. Copolymer/PDMS blends. For example, amphiphilic copolymers can be incorporated into PDMS as surface-active additives by mixing. Martinelli et al. [247] prepared surface-active
copolymers of styrene containing a polysiloxane side chain and a triethylene glycol monomethyl ether-modified perfluorostyrene through a free-radical copolymerization (Fig. 15a). These surfacactive copolymers were mixed into a PDMS matrix to produce an amphiphilic blend film. Under atmospheric conditions, the film surface was covered by both siloxane and oxyethylenic chains in a random distribution. After immersion into water, a reconstruction of the surface occurred, and the amount of the hydrophilic oxyethylenic segments on the surface increased. This contributed to better resistance against zoospores of U. linza and superior fouling-release properties of sporelings compared to standard hydrophobic PDMS films. In another exemplary work, Oliva et al. [138] found that such surfaces can not only repel spores. They demonstrated that dispersion of amphiphilic block copolymers in PDMS enhanced the resistance to different barnacle species (i.e., B. amphitrite and Balanus improvisus). However, it should be considered in the future development of such coatings that pentfluorophenyl (or tetrafluorophenyl) derivatives are not stable to chemical reaction.

4.3.1.2. Crosslinked blends. However, embedding a surface-active compound within a polymer matrix can suffer from the drawback of additive leaching out from the polymer matrix after prolonged contact with water, thus causing a loss in efficiency of the system and environmental problems [257]. One approach to overcome this drawback is to covalently link the surface-active component to the polymer matrix. For example, Martinelli et al. [258] prepared an amphiphilic PDMS-based film through a sol-gel condensation crosslinking reaction by using bis-silanol terminated PDMS as a matrix, with hydrophilic polyoxyethylene triethoxysilane and hydrophobic 1H,1H,2H,2H-perfluorooctyl trimethoxysilane as surface-active agents. The degree of surface amphiphility could be modified by changing the relative proportion of polyoxyethylene triethoxysilane and 1H,1H,2H,2H-perfluorooctyl trimethoxysilane in the formulation.

Likewise, Zhao et al. [248] used crosslinking to stabilize their coating. They crosslinked different amounts of hydrophilic- active poly(N-vinyl-2-pyrrolidone-co-methyl methacrylate-co-butyl acrylate-co-2-hydroxyethyl methacrylate) (PNMBH) with PDMS (Fig. 15b). The PNMBH was synthesized through free radical polymerization based on poly(N-vinylpyrrolidone). As a result, compared to pure PDMS, the PNMBH-PDMS coatings decreased the amount of adhesion of fibrinogen by 82%, of Staphylococcus aureus by 97%, and of diatoms by 97%. Their composite exhibited good anti fouling performance for 4 months in the marine field test.

Wang et al. [249] used another approach and proposed a coating based on PDMS and pentaerythritol tetrakis (3-mercaptopropionate). They crosslinked PDMS terminated by reactive allyl groups with pentaerythritol tetrakis (3-mercaptopropionate) via click chemistry, followed by a surface zwitterionization with 3-BPA to form a dual-mode network. The composite showed increased resistance to proteins (bovine serum albumin and lysozyme) and diatoms (Phaeodactylum tricornutum) attachment.

4.3.1.3. Surface-grafted PDMS. Amphiphilic coatings can also be synthesized by grafting the hydrophilic components onto the PDMS surface. For example, Kulisha et al. [250] fabricated PDMS-based amphiphilic polymers grafted with poly(co-acrylate) through a plasma-assisted method (Fig. 15c). Compared to pure PDMS, the modified surfaces exhibited improved anti fouling and fouling-release properties with a 92% reduction of the initial attachment density of zoospores of the green alga U. linza and a 55% increase in the number of diatoms removed.

4.3.1.4. Coatings with improved adhesion. In general, the poor adhesion of PDMS coatings to a substrate (e.g., a ship hull) due to their intrinsically low surface energy is well known and can be improved by various approaches (e.g., additive incorporation and chemical modification) [39,136]. In the field of amphiphilic coatings, Wang et al. [254] developed a self-adhesive PDMS-based polymer by the incorporation of dopamine methacrylamide. The full fabrication process consisted of the copolymerization of dopamine methacrylamide, mercaptopropyl methylsiloxane-dimethylsiloxane, and poly (ethylene glycol) diacrylate via UV

Fig. 14. Working principle and fabrication of amphiphilic coatings. a) Organisms that tend to settle on hydrophobic or hydrophilic surfaces can be repelled as soon as the areas available for settlement get below a critical size. b) Amphiphilic coatings consist of a base polymer, hydrophobic and hydrophilic moieties. The functional moieties can be blended, crosslinked, or grafted to the base polymer. 
Fig. 15. Examples of amphiphilic biofouling control coatings. a) Synthesis of the surface-active copolymers of styrene [247]. Copyright 2016. Adapted with permission from Elsevier. b) The formation of the amphiphilic coatings using PNMBH crosslinked with PDMS matrix at room temperature [248]. Copyright 2019. Adapted with permission from Elsevier. c) PDMS-based amphiphilic polymers grafted with poly(co-acrylate) [250]. d) The preparation of biomimetic amphiphilic PDMS-based crosslinked antifouling coatings [254]. Copyright 2019. Adapted with permission from Elsevier. e) Chemical formulas of the grafted polymers: P(PEGMA), P(PDMSMA), PDMS-COOH. False-color SEM image of the SiO2-P(PEGMA)/PDMS-Janus particles layer [255]. Copyright 2016. Adapted with permission from the American Chemical Society. f) Synthesis of amphiphilic polymer ((SBS-co-BD-FT-LSR)-r-PEG) [256].

Photo-crosslinking (Fig. 15d). The heterogeneous nanoscale surfaces exhibited effective resistance to nonspecific protein adsorption and *P. tricornutum* attachment.

4.3.1.5. Coatings for large-scale applications. Kirillova et al. [255] developed an amphiphilic coating suitable for large-scale applications by using amphiphilic Janus particles with an inorganic core and hydrophilic/hydrophobic polymeric shells. The shells consist of hydrophilic poly(ethylene glycol) methyl ether methacrylate) (P(PEGMA)) and hydrophobic PDMS, or poly(monomethacryloxypropyl-terminated polydimethylsiloxane) (P(PDMSMA)) grafted at the opposite sides of the core (Fig. 15e).
These coatings can be easily prepared by solvent casting or spraying of the particle suspension, and applied to surfaces on a large scale.

### 4.3.2. PEG-based amphiphilic coatings

PEG is hydrophilic and can resist cell adhesion and protein adsorption due to the low interfacial energy with water (<5 mN.m\(^{-1}\)), which makes the intramolecular forces between the biomacromolecules and the substratum thermodynamically unfavorable. To fabricate amphiphilic surface-active (co)polymers, PEG can be combined with a hydrophobic component (mostly fluorinated materials) [245]. Similar to PDMS, fluorinated polymers have low surface free energy, which can reduce polar and hydrogen bonding interactions with the bio-adhesives used by fouling organisms. As summarized by Martinelli et al., PEG/fluorinated-based amphiphilic polymers can be produced by different strategies, such as multilayers of fluorinated/PEGylated polypeols, UV photo-crosslinking of mixtures containing PEG and fluorinated macromonomers, crosslinking of PEG with hyperbranched fluoropolymers, and self-assembly of fluorinated/PEGylated copolymers blended with an elastomeric matrix [247, 258-263]. However, since most of the antifouling studies on PEG-based amphiphilic coatings have been conducted under laboratory conditions with selected microorganisms, field experiments are needed to validate their performance in the complex marine environment [240, 247, 264].

For example, recently, Li et al. [256] synthesized an amphiphilic polymer coating from polystyrene-polybutadiene-poly styrene (SBS), vinyl fluoride silicone (BD-FT-LSR), and PEG (Fig. 15f). The coating was proven to possess good antifouling properties against algae and easy-to-clean properties after 6-month marine antifouling testing.

### 4.3.3. PDMS-PU-based amphiphilic coatings

To overcome the disadvantages (low mechanical strength and poor adhesion to substrates) of PDMS-based coatings, the self-stratified siloxane-polyurethane (SiPU) coating system has been developed and investigated by the research group of Webster since 2005 [265-272]. The coating system contains a two-component PU (prepared from a polyl and a polysiloxane) and a functional PDMS which reacts with isocyanates. During film formation, the PDMS component segregates spontaneously to the surface due to its low surface energy, giving rise to fouling-release properties of the coating system. The bulk of the coating is dominated by PU, providing good mechanical strength and high adhesion to substrates [273].

To further improve the fouling-release properties of the SiPU coatings, Galhenage et al. [274] incorporated amphiphilic additives into the SiPU coatings. The amphiphilic additive was synthesized by reacting nonfunctional PEG and PDMS with isophorone disiocyanate trimer. The amphiphilic coating showed excellent fouling-release performance toward bacteria (Cellulophaga lytica), the diatoms (N. incerta), and the green algae (U. linza), as well as good macrofouling (barnacle Amphibalanus amphitrite and mussel Geukensia demissa) release. Subsequently, Rahimi et al. [275] investigated the effect of the concentration of the same amphiphilic moieties on fouling-release properties of the PU-based coating. By incorporating varying amounts of amphiphilic additive in PU, the critical amphiphilic concentration was obtained by evaluating the fouling-release properties of the coating using U. linza, C. lytica, and N. incerta as the test organisms. With increasing the amount of the amphiphilic additives, the fouling-release performance of the coating was improved and plateaued once the critical amphiphilic concentration is attained in the coating system.

Moreover, Rahimi et al. [276] prepared another amphiphilic additive where highly incompatible blocks of hydrophobic PDMS and hydrophilic poly(sulfobetaine methacrylate) were connected, using ARGET ATRP (activators regenerated by electron transfer atom transfer radical polymerization) controlled radical polymerization technique. When mixing the amphiphilic additive into the SiPU coating, the presence of self-migrated amphiphilic additive on the coating surface improved its fouling-release performance against macroalgal spores (U. linza) and barnacles (A. amphitrite). It was further shown that the molecular weight of the hydrophobic PDMS block should be considered when preparing the amphiphilic additive, while the size of the hydrophobic poly(sulfobetaine methacrylate) block may not influence the effectiveness of the additive. However, the hydrophilic portion of 50% to 80% was suggested to provide the coating with the desired amphiphilicity. Benda et al. [277] fabricated amphiphilic additives via hydrosilylation using various polymethylhydroisiloxanes and allyl-terminated PEG monomethyl ethers of varying molecular weights. The SiPU coating with the incorporation of the amphiphilic additives showed better antifouling and fouling-release properties compared to the reference SiPU coating. The best performance was shown by the SiPU coating containing amphiphilic additive with a low grating density of relatively high molecular weight PEG chains.

In addition to the above-discussed works, Padé and Webster [273] have recently reviewed the development of the SiPU coatings over the last 20 years and discussed the influence of various composition variables on the properties of SiPU coatings as well as different approaches in the modification of the SiPU coatings.

### 4.3.4. Peptide and peptoid modified amphiphilic coatings

As discussed above, amphiphilic coatings can be designed by incorporating hydrophilic and hydrophobic moieties into a base polymer, and the antifouling performance is strongly related to the surface composition [278]. However, precise control of the amount and distribution of the hydrophilic and hydrophobic moieties on the polymer surface remains challenging [279, 280].

#### 4.3.4.1. Peptide-based amphiphilic coatings

In this perspective, peptides gained enormous attention as the building blocks for the amphiphilic components due to their tuneable structural characteristics and additional immanent antifouling properties against biomolecules, bacteria, and other organisms [281]. For example, by controlling the exact order of the addition of the amino acid building blocks and therefore the location of the hydrophilic and hydrophobic components in the peptide chain backbone, peptides can be exploited to finely and systematically tune the amphiphilic balance of the surface, thereby optimizing the antifouling properties [245].

To investigate how the polarity range and the sequence order of side groups affect the antifouling properties, Calabrese et al. [240] synthesized different oligopeptide sequences, which were then attached to the polystyrene-block-poly(dimethylsiloxane-vinylmethylsiloxane) (PS-b-P(DMS-VM)) diblock copolymer through thiol-ene click chemistry. It has been shown that the order of the amino acids in an oligopeptide affects the surface wettability, but does not significantly affect the resistance to proteins and spores. For future work, it has been proposed to increase the size of the side groups when investigating the influence of the order of the amino acids on the antifouling and fouling-release surface properties.

Although peptide-modified coatings show promising results for introducing amphiphilicity, peptides remain expensive and challenging to produce [89]. Being a structural analog of peptides, peptoids can be produced via a submonomer solid-state synthesis, which allows for higher yields and simple incorporation of more diverse chemistries [282]. Peptoids (Fig. 16a) are composed of N-substituted repeat units, in which the side chain is linked to the nitrogen atom of the peptide backbone, rather than to
the α-carbon as in the corresponding amino acid. The N-substituted glycine backbone is more resistant to proteolytic degradation, making peptoids more suitable for biological applications.

4.3.4.2. Peptoid-based amphiphilic coatings. More studies have been conducted on the design and fabrication of peptoid-modified amphiphilic coatings to understand the relation between the surface structure (e.g., arising from the backbone structure and monomer sequence) and antifouling properties.

To investigate how the sequence of hydrophilic and hydrophobic moieties in peptoids affects the surface structure and marine antifouling, Zoelen et al. [285] prepared different polypeptoid sequences containing two functional groups: a hydrophilic...
N-[2-methoxyethyl]glycine (Nme) unit and a hydrophobic N-(heptafluorobutyl)glycine (NF) unit (Fig. 16b). Then the peptoids were attached to the polystyrene-b-poly(ethylene oxide-co-allyl glycidyl ether) (PS-b-P(EO-co-ACE)) scaffold via thiol-ene click chemistry (Fig. 16c). It was shown that the sequence of the moieties and the position of the fluorinated units in the polypeptoid chain affected the surface chemistry, surface structure, and thereby the antifouling and fouling-release performance. However, it remains unclear whether the difference in antifouling performance is due to the difference in surface chemical composition, surface structure, or a combination of the two (Fig. 16d).

Although sequence-dependent surface structures of peptoids have been well investigated, their molecular structures under aqueous conditions relevant to marine fouling have seldom been studied. By applying sum frequency generation vibrational spectroscopy, Leng et al. [280] investigated the surface structure and hydration of a series of amphiphilic polypeptoid coatings with different sequences in air and water. Their research indicated that surface coverage of the hydrophilic Nme units in the air was affected by both the number and position of the hydrophobic NF units in the peptoid chain and was negatively correlated with the surface concentration of the fluorine element. It was shown that the presence of the Nme groups on the surface and the ability of the polymers to order and strongly bond with interfacial water molecules determined their antifouling properties, while the surface restructuring rate upon contact with water affected their fouling release behavior (Fig. 16e).

By making sequence-defined oligomer side chains, Patterson et al. [264] investigated the effects of the backbone chemistry on the marine antifouling performance. In their study, the PDMS- and PEO-based block copolymer coatings were functionalized with amphiphilic, surface-active, and sequence-controlled oligomerpertide and oligopeptoid side chains (Fig. 16f). It was shown that the lack of a hydrogen bond donor in the peptoid backbone may lead to a decrease in the adhesion strength of sporelings on these surfaces (Fig. 16g).

A similar conclusion was drawn by Barry et al. [284]. An amphiphilic peptoid was prepared, which contained functional groups similar to those typically on a hydrogen-bonding peptide backbone. This peptoid and a non-hydrogen-bonding peptoid analog were incorporated as side chains into PDMS via thiol-ene click reaction (Fig. 16h). It was shown that the amphiphilic peptoid lacking hydrogen bond donors possessed better resistance against marine fouling such as U. linza and N. incerta than hydrogen-bonding analogs (Fig. 16i).

In summary, amphiphilic coatings were designed to combine the antifouling and fouling-release properties of purely hydrophilic and hydrophobic coatings. Therefore, such surfaces are expected to not only prevent the microfouling attachment (e.g., protein, bacteria, diatom), but also decrease the macrofouling (e.g., barnacle) adhesion strength. By using amphiphilic polymers, the surface activity of the coatings can be tuned at the molecular structures. However, the good resistance to and easy release of the wide variety of proteins and marine organisms under real conditions, as well as the mechanical stability and durability for long-term effectiveness of amphiphilic coatings, still need further evaluation and investigation. Additionally, for peptide and peptoid modified coatings, the high cost should be taken into consideration when used in the marine field.

5. Self-renewable coatings

Traditionally, self-renewable coatings are antifouling coatings, which exhibit a controlled biocide release triggered by the gradual degradation taking place at the surface of the polymeric host matrix. The term self-renewal hereby is related to the renewal of the antifouling performance over time and indicates the enhanced service-life of such coatings. A more advanced understanding of the term self-renewal, which recently emerges with the desire for more biofriendly solutions, represents the ability of biofouling reduction solely via the peeling-off mechanism offered by the degradation procedure (please note the difference to the fouling-release mechanism originating from hydrophobic surfaces described in Section 4.1).

Generally, within the category of self-renewable coatings, three different subtypes can be distinguished according to the degradation mechanisms and their point of interaction within the polymer chain structure:

(i) Self-polishing coatings hydrolyze at the surface when in contact with sea water via the hydrolyzation of their side chains. This mechanism is commonly based on side chains containing carboxylate moieties. Simultaneously, the hydrolyzed surface can gradually erode and get detached layer by layer via external shear forces (Fig. 17a).

(ii) Degradable coatings gradually degrade in sea water without the necessity of shear forces since they self-disassemble via hydrolyzation and biodegradation of their backbone chains. Recently developed degradable coatings are often based on polyurethanes (Fig. 17b).

(iii) The combination of self-polishing and degradable properties (Fig. 17c).

5.1. Self-polishing coatings: renewal via side-chain cleavage

Self-polishing coatings originally came up as an improved variant of the highly toxic organotin-based coatings (Section 1) since they allow for a controllable and constant biocide release rate and thereby an enhanced product lifetime. Initially, at the early stage of the application of organotin antifouling coatings, organotin compounds were physically mixed into the coating matrix instead of bonded chemically to it. As a result, the biocide leached freely from the matrix without keeping a constant release rate, which negatively affected the service lifetime of the coatings [286]. To achieve a constant leaching level of the organotin compounds, numerous studies have been conducted on the linkage between the biocide and polymer matrix [286,287]. Research mainly focused on the polymerization between organotin compounds and acrylate compounds following a typical working principle: When the coating surface got in contact with seawater, organotin compounds were released via hydrolysis. Subsequently, the outer layer of coatings with the hydrophilic carboxylate group was eroded by seawater when subjected to a shear force (e.g., during movement of a ship) and finally detached. Thus, a fresh acrylate surface was exposed to the seawater again. As a result, the organotin compounds were slowly released from the polymer matrix at a constant rate. Additionally, the coating surface was smoothed due to its renewal. The whole process was defined as “self-polishing” and coatings with a similar release and erosion process were named self-polishing coatings accordingly.

Even if the self-polishing organotin-based antifouling coatings have ever been the most effective method to inhibit marine biofouling since the 1970s [35], organotin compounds were confirmed to be highly toxic to a wide range of marine organisms [288,289] and the International Maritime Organization globally prohibited its application since 2008 [286]. Nevertheless, the corresponding self-polishing mechanism could be imitated to develop novel, organotin-free coatings. These tin-free self-polishing antifouling coatings usually contain copper, zinc, and silicon groups incorporated into the polymer matrix, and the self-polishing effect is achieved by the hydrolysis reaction between pendant functional groups and the ions present in seawater such as Na⁺, Cl⁻, and...
OH⁻ (Fig. 18a). In general, modern self-polishing antifouling coatings can contain (i) metal-based, (ii) non-metallic, or (iii) derivatives of natural antifouling agents.

5.1.1. Computational representation of the self-polishing process

Kwon et al. [117] explained the decomposition mechanisms of self-polishing polymers (TBT, zinc methacrylate (ZMA), copper methacrylate (CMA), and triisopropylsilyl acrylate (TIPSA)) by density functional theory calculations (Fig. 18b). As illustrated in Fig. 18c, the decomposition process of self-polishing polymers was divided into three steps being characterized by an initial, transition, and final degradation state. At the initial stage, Na⁺ preferably was adsorbed at the oxygen sites of the self-polishing polymers. Meanwhile, Cl⁻ and OH⁻ were oriented to the pendant groups (i.e., Sn, Zn, Cu, or Si atoms, etc.). During the transition stage, decomposition of the molecule occurred by insertion of the dissociated ions from NaCl and NaOH between the O and the other pendant groups. After the decomposition, the whole system entered the final stage in which the O atoms in the backbone chain and the Na⁺ cations were strongly connected to each other as well as the positively charged pendant groups (i.e., Sn, Zn, Cu, or Si atoms, etc.) in the functional group and the anions (Cl⁻ and OH⁻).

5.1.2. Zn-based antifouling monomers

Recently, the research on metallic antifouling and self-polishing monomers focused on monomers related to zinc. However, the commonly used zinc methacrylate monomers, due to their high glass transition temperature, restrict the fluidity of the paint and thereby cause adverse effects on the storability and stability [293, 294] of the antifouling paints. This is why researchers were developing derivatives with improved properties.

For example, Chen et al. [293] designed zinc-based acrylate copolymers with improved stability by using bifunctional zinc acrylate monomers as new self-polishing monomers and methyl methacrylate, ethyl acrylate, and 2-methoxyethyl acrylate as comonomers. The erosion tests and polarizing optical microscopy images confirmed the self-polishing process of the copolymers under artificial seawater conditions. The viscosities of copolymers remained at approximately 70 KU for 5 months, which indicated that the prepared copolymers had high storage stability. Kim et al. [294], however, based their self-polishing monomer on propanoate. They copolymerized zinc 3-(allyloxy)propanoate with methyl methacrylate, 2-hydroxyethyl methacrylate, and ethyl acrylate. The self-polishing effect of these copolymers was confirmed by thickness measurements.

5.1.3. Non-metallic antifouling monomers

Conventional self-polishing coatings are generally based on acrylate-based copolymers with heavy metal substitutes (Zn-, Cu-, etc.). If the organometallic compounds are continuously released into the seawater during the self-polishing process, the accumulation of these compounds will also be harmful to marine organisms in the future. Therefore, researchers aim to design nonmetallic self-polishing monomers.

For example, Wang et al. [290] synthesized quaternary ammonium-modified SiO₂ nanoparticles (QAS-SiO₂) and mixed them into a self-polishing polymer with a trisopropylsilyl methacrylate side chain (Fig. 18d). Compared to the unmodified SiO₂, QAS-SiO₂ exhibited better compatibility with the self-polishing polymer, and the coating formed no cracks after 30 days of immersion in artificial seawater. Moreover, compared to the pure self-polishing polymer and the one including SiO₂, those with different amounts of QAS-SiO₂ showed higher sterilizing rates
Fig. 18. Mechanism and examples of self-polishing coatings. a) Typical reaction route of self-polishing polymers with seawater. b) Density functional theory calculations of the molecular model and simplified backbone chain of: (i) TBT, (ii) ZMA, (iii) CMA, and (iv) TIPSA, and c) the corresponding stages of their decomposition mechanisms in seawater [117]. Copyright 2020. Adapted with permission from Elsevier. d) Preparation of self-polishing coating containing QAS-SiO₂ and its antifouling mechanism in seawater. [290] Copyright 2020. Adapted with permission from Elsevier. e) Antifouling process of acrylate boron fluorinated polymers [291]. Copyright 2019. Adapted with permission from the American Chemical Society. f) The antifouling mechanism of the acrylate coatings suspending the indole derivative from the side chain [292]. Copyright 2019. Adapted with permission from Elsevier.
(91.5–97.4%) in the bacteria-killing assay due to the excellent bactericidal activity of QAS-SiO$_2$. In the bacteria adhesion test, compared to the blank glass slide, the self-polishing polymers with QAS-SiO$_2$ reduced the fraction of bacterial density by 91.0%. This indicated that the self-polishing polymers with QAS-SiO$_2$ exhibited antibacterial property through a synergistic effect of self-renewal ability and antifouling function.

Next to SiO$_2$ nanoparticles, organic boron polymers also possess antifouling properties, and nonmetallic acrylate boron polymers (ABPs) that are comprising self-polishing properties have been synthesized. For example, Li et al. [295] synthesized such ABPs by a protonolysis reaction of acrylate acid polymers and pyridine-tri phenylborane resulting in polymers with an acrylate backbone and pyridine-phenyl borane side chains. The antifouling performance of these polymers emerged from the hydrolysis of the diphenyl borane pyridine groups. It was shown that there was a reduced Nitzschia closterium diatom attachment compared to the blank glass slide. Furthermore, comparing different ABPs with varying pyridine-tri phenylborane content indicated that the antifouling performance decreases with decreasing pyridine tri phenylborane content due to a decreasing hydrolysis rate. Only negligible fouling organisms were found on the samples after immersion for 12 months, while some hard-shell organisms grew on the blank plate.

Although the above acrylate boron polymers showed a certain degree of antifouling property, the polymers exhibited poor performance against slime and silt in the ocean raft test. To improve the antifouling property, Li et al. [291] synthesized another series of acrylate boron polymers with amphiphilic properties by introducing fluorinated monomers. The amphiphilic polymers exhibited a better antifouling property in the diatom settlement test and field immersion compared to the pure ABPs. This was attributed to the combination of self-polishing and amphiphilic repulsion effect (Section 4.3). The proposed model of this antifouling process is shown in Fig. 18e.

5.1.4. The derivatives of natural antifouling monomers

Former antifouling coatings used to possess a very good performance due to the synergy of the self-polishing effect and the strong biocidal activity of the contained tributyltin compounds. In comparison, the antifouling performance of tin-free self-polishing polymers is not as effective. To improve this situation, one approach is to incorporate environmentally friendly bioactive substances [296,297].

For example, Feng et al. [292] introduced an indole derivative to self-polishing copolymers to enhance their antifouling performance (Fig. 18f). Indole is an aromatic, heterocyclic amine that can be found in various natural materials such as serotonin and melatonin. The acrylate coatings supplemented with the indole derivative structure in the side chain were prepared by the free radical polymerization of N-(1H-2-phenyl-indole-3-ylmethyl) acrylamide, butyl acrylate, ethyl acrylate, acrylic acid, and methacrylic acid. The modified self-polishing coatings were evaluated in terms of the polishing performance and antifouling property. After introducing the indole derivative, the self-polishing property was still maintained. However, the more indole derivatives introduced to the acrylate resins, the less ratio of carbohydrate moieties were in the resins. As the carbohydrate moieties play a determinant role in the self-polishing process, the self-polishing rate of the acrylate resins containing indole derivatives was reduced with an increase in the amount of indole derivatives. The biological simulation tests showed that the acrylate coatings containing the indole derivative exhibited a better antifouling performance than the unmodified ones.

Tributyltin-free self-polishing coatings have been investigated and used since the ban of organotin application. Although these antifouling coatings have been commercially available due to the controllable polishing rate, there are some drawbacks:

(i) After exposure to seawater, the outer layer hydrolyzes and becomes hydrophilic. To expose a fresh surface, this hydrophilic layer needs to be eroded and removed by some shear force (e.g., during the movement of a ship) at first. Therefore, these coatings can lose their effective antifouling performance under static conditions.

(ii) To ensure good antifouling performance, there are always bio- cidal ingredients incorporated into the self-polishing coatings. These side chains, which usually contain Zn and Cu elements, are released into the seawater, resulting in the accumulation of these elements in the marine environment. Meanwhile, these copolymers may lead to an accumulation of microplastics due to the non-degradable main chain. This issue may probably lead to the prohibition of such self-polishing coatings in the future.

5.2. Degradable coatings: renewal via backbone cleavage

Self-polishing copolymers with biocides can exhibit a long-term antifouling period of up to 5 years [34,287]. However, due to the non-degradability of the self-polishing polymers’ mainchain, the post-hydrolysis polymers can also persist in the marine environment for long periods. In a nutshell, these coatings release microplastics that negatively affect marine ecosystems [289,299]. As the laws and regulations on environmental protection become more and more stringent, the application of self-polishing polymers may be restricted in the future. This is why, in recent years, there has been growing interest in degradable polymers. In contrast to self-polishing polymers, the backbone chain of degradable polymers can be decomposed by the enzymatic action of microorganisms (e.g., bacteria, fungi, and algae) [300]. In addition, the polymer main chains can also be cleaved by chemical hydrolysis [301]. This way, i.e., under the dual effect of hydrolysis and biodegradation, the polymer can be degraded into small molecules or low molecular weight substances [302]. In summary, coatings based on degradable polymers offer two basic advantages over self-polishing coatings:

(i) The decomposition products are of low molecular weight and do not lead to an accumulation of microplastics in the seawater.

(ii) The detachment of the outmost layer takes place continuously by degradation and decomposition, thus, guaranteeing a surface self-renewal effect even under static conditions. This effect alone can reduce the attachment of fouling organisms. Additionally, as in the case of self-polishing coatings, degradable polymers can be applied as antifouling carriers with a controllable biocide release.

Recently, the research on degradable coatings focuses on polyurethane-based copolymers. Polyurethane (PU) has been a versatile polymer in several industrial applications (e.g., coatings, adhesives, elastomers, etc.) since the 1950s [303]. Because their degradation characteristic fulfills the requirements of marine environmental protection, PU-based paints are gradually applied in the marine sector as degradable antifouling coatings [304]. In general, PUs are synthesized by using diisocyanates, diols, chain extenders, and catalysts [305]. To achieve the desired properties, different diols can be used to synthesize PUs with different structures and functions. The long-chain diols used in the production of PUs can be divided into four categories: polyester diols, polycarbonate diols, polycaprolactone diols, and polyester diols [306]. According to the different diols, polyurethane can be divided into (i) polyester polyurethane of consistent polyester diols and (ii) polyester polyurethane of consistent polycarbonate diols, polycaprolactone diols, or polyester diols. Compared with polyester
polyurethane, polyester polyurethane is more easily degraded by microorganisms and water in the environment [307,308]. Here, the hydrolysis of the ester bond as well as biological degradation plays a joint role in the degradation process. Thus, the researches of degradable coatings focus on polyester polyurethane. Fig. 19 displays the chemical structures of the degradable polymers that are reviewed in the following.

5.2.1. Polyurethanes based on polycarbonate diols

For example, Chen et al. [309] prepared a thermoplastic poly(propylene carbonate) polyurethane (Structure 1 in Fig. 19) in a two-step condensation polymerization. Tin 2-ethylhexanoate was used as catalyst and 1,4-butanediol as a chain extender. The poly(propylene carbonate) segments thereby served as degradable moieties. It was found that poly(propylene carbonate) polyurethane can be degraded in the presence of lipase Pseudomonas sp. and that the degradation rate increases with the decrease of the molecular weight of the copolymers. The biofouling test indicated that fewer organisms (e.g., barnacles) colonized on the degradable poly(propylene carbonate) polyurethane compared with the panels with no copolymer.

5.2.2. Polyurethanes based on polycaprolactone diols

Polycaprolactone (PCL) can degrade in the environment within several months to several years depending on the molecular weight, the crystallinity of the polymer, and the degradation conditions [310,311]. Ma et al. [312] combined degradable PCL with the antifouling properties of butenolides. They incorporated 5-octylfuran-2(5H)-one (a butenolide) from the marine bacteria Streptomyces spp. into a poly(ε-caprolactone) based polyurethane (PCL--PU). The PCL--PU (Structure 2 in Fig. 19) was synthesized by polyaddition. Dibutyltin dilaurate was thereby used as catalyst and 1,4-butanediol as chain extender. The enzymatic degradation experiment showed that the degradation amount of PCL--PU gradually increased and stabilized after introducing the lipase Pseudomonas sp. Meanwhile, the hydrolytic degradation test showed that the weight of PCL-PU started to decrease in artificial seawater and natural seawater after immersion for 3 days. Additionally, the corresponding mass-loss was particularly higher during immersion in natural seawater. The difference in degradation between artificial and natural seawater may be caused by the presence of marine microorganisms or enzymes in the natural marine environment since they can induce the biodegradation of the ester bond in the polymer. The PCL--PU polymer with butenolide exhibited strong antifouling ability for over 3 months.

In contrast, Azemar et al. [313] suggested hybrid antifouling coatings combining degradable, biocidal, and superhydrophobic components. Thereby, they focused on the investigation of linear triblock copolymers as the binder material in their multifunctional antifouling paints. The coatings were synthesized by ring-opening polymerization using dibutyltin dilaurate as a catalyst. The triblock copolymers (Structure 3 in Fig. 19) included poly(ε-caprolactone) external blocks and a polydimethylsiloxane (PDMS) core block. Three types of copolymers with different ratios of PCL and PDMS were prepared and defined as PCL 50, PCL 66, and PCL 90 (molar ratio of PCL--PDMS--PCL: 25-50-25, 33-33-33, and 45-10-45, respectively). PCL 50 had the lowest crystallinity among three copolymers, which indicated that the crystallinity decreases with increasing PDMS content. The paint PCL 50s, PCL 66s, and PCL 90s were formulated with a binder (PCL 50, PCL 66, and PCL 90), solvents, fillers, and additives. As SEM images revealed, large cracks emerged on the paint PCL 90s surface during drying. This was assigned to the high crystallinity and lack of elasticity of the PCL 90. The quantitative hydration study showed that the hydration rate of the paint PCL 50s (27%) was more than that of paint PCL 66s (23%). The maximum degradation rate of paint PCL 50s and 66s was reached after 250 and 300 days, respectively. The difference was explained by the higher hydration rate of the paint PCL 50s in combination with the faster degradation rate of the PCL 50. Generally, the paint with a slower hydration rate needs more time to reach the maximum degradation of the binder. In the field test, some algae were present on the antifouling paint surfaces while the control group was completely colonized by algae after 24 weeks.

5.2.3. Polyurethanes based on polyester diols

Chen et al. [314] prepared polyurethanes (Structure 4 in Fig. 19) with three different degradable polyester segments: (poly(ethylene adipate) (PEA), poly(1,4-butylen adipate), or poly(1,6-hexamethylene adipate)). They used dibutyltin dilaurate as a catalyst and 1,4-butanediol as a chain extender. Apart from the relatively rapid weight loss at the initial stage (due to the release of low molar mass components), the degradation of modified polyurethanes was achieved at a constant rate after 7 days. The PU containing PEA had a higher degradation rate than the PU containing poly(1,4-butylen adipate) or poly(1,6-hexamethylene adipate), since the former had lower crystallinity. It is well known that the degradation rate can be influenced by the crystallinity of polymer since molecules can penetrate more easily into amorphous regions. Namely, the degradation rate of the polymer increases with the decrease of crystallinity. The amount of degradation increased with a higher proportion of the PEA soft segment in the PU, and the PU containing PEA (80%) showed the best antifouling performance.

5.3. Combination of self-polishing and degradation

Although the antifouling property of self-polishing coatings is limited under static conditions, the mechanism of side-chain hydrolyzation is still of value. Fig. 17 shows the different mechanisms of (i) self-polishing coatings, (ii) degradable coatings, and (iii) their combination with main-chain degradation and side-chain hydrolyzation.

To achieve the antifouling performance of the coatings by the dual effect of degradation and side-chain hydrolyzation, Zhou et al. [315] synthesized a copolymer (Structure 5 in Fig. 19) from 2-methylene-1,3-dioxepane (MDO), tributylisilyl methacrylate (TBSM), and methyl methacrylate by a ring-opening copolymerization. The MDO and TBSM moieties endowed the polymer with a degradable backbone and hydrolyzable side groups, respectively. With the increase in MDO content (from 8 wt% to 23 wt%), the mass loss of corresponding copolymers increased in the hydrolytic degradation. This result was attributed to the scission of the ester linkages, which made the polymer easier to dissolve into seawater. However, the opposite happened when the MDO content of the copolymer was higher than 23 wt% (from 38 wt% to 47 wt%). This discrepancy was explained by the fact that hydrolyzation got difficult when the amount of the TBSM decreased simultaneously. Accordingly, the mass loss of copolymers depended on the combination of the degradation of their backbone and the hydrolysis of tributylisilyl side group. Therefore, the degradation rate could be regulated by the molar ratio of the ester units in the backbone to the silyl ester side groups.

Ma et al. [316] investigated the influence of the side chain length and ester group density on the self-polishing and degradation properties of a PU-based coating. They prepared different PU (Structure 6 in Fig. 19) with the degradable polyester segments (poly(ε-caprolactone) (PCL), poly(L-lactide) (PLA) or poly(ethylene adipate) (PEA)) in the main chain and hydrolyzable poly(triisopropylsilyl) acrylate) side chains. Dibutyltin dilaurate was used as catalyst and 1,4-butanediol as chain extender. To optimize the degradation performance, the PUs with the same main chains
Fig. 19. Chemical structures of some examples of degradable polymers.
(PCL segment) but different side chain lengths were defined as PU-S336, PU-S1400, and PU-S2600 (sequentially increasing side chain length). The PUs with the same side chain length but different types of main chains were defined as PU-PCL, PU-PEA, PU-PLA. The ester group density increased in the order: PCL < PEA < PLA. For the PUs with the same main chains (PU-S336, PU-S1400, and PU-S2600), the degradation rate was improved when the side chain length increased. The higher content of silyl ester groups in the PUs with longer side chains could have led to the increased hydrolysis rate. For the PUs with the same side chain length, the hydrolysis rate decreased in the following order: from PU-PLA to PU-PEA and to PU-PCL. The hydrolysis rate of polyester rose with the increase in the ester group density (PCL < PEA < PLA). As expected, the PU with the higher polyester density showed better antifouling property (the fouling on the surface increased in the order: PU-S2600, PU-S1400, and PU-S336; PU-PLA, PU-PEA, and PU-PCL). These results confirmed that the hydrolysis rate contributed to the antifouling performance in the degradable polymers.

Apart from the molecular weight, crystallinity, or ester density [317], the degradation rates of copolymers are also influenced by other factors such as the initial pH value or temperature of the external environment [318]. However, these external factors remain relatively stable in seawater and they are assumed to have less impact on the degradation of copolymers. Despite the promising antifouling properties of degradable copolymers, some basic requirements remain unfulfilled so far, which research should try to meet in the near future:

(i) **Environmentally friendly fabrication routes:** Degradeable polymers can be synthesized through condensation or ring-opening polymerization, catalyzed by metal alkoxides, metal carboxylates, or ionic initiators. This may potentially cause harm as most metal-based catalysts are toxic and it is difficult to remove them completely from the coating during the purification process [319,320].

(ii) **Table 2 shows the common adjuvants for polyurethane synthesis and their relative toxicities [321].** Calcium and magnesium-based catalysts and lipases are alternatives to the abovementioned traditional catalysts due to their reduced toxicity [310].

(iii) **Matching degradation and fouling rates:** The relationship between the degradation rate and fouling adhesion rate generally needs further investigation, and more effort should be put into the careful matching of these two parameters in the future. If the coatings degrade too slowly, marine fouling organisms will attach to the surface and long-term efficiency and durability of the coatings cannot be guaranteed.

### 6. Coatings containing antifouling agents

Commercial biofouling control coatings commonly contain antifouling agents, i.e., biocidal compounds which are supposed to kill or deter undesired biofouling organisms. In the 19th and early 20th centuries, heavy metals (e.g., copper, arsenic, mercury) were used as antifouling agents [322]. Until the 1960s, TBT emerged as the most efficient biocide [323,324]. Despite being effective in preventing marine organisms’ attachment, these antifouling agents were found to be harmful to non-target organisms and have a significant impact on the marine ecosystem [18,325]. Therefore, research and development strive to find alternative antifouling agents that meet the requirements for adequate properties while complying with strict environmental rules [111–113]. Thereby, antifouling agents can be classified into (i) natural agents that are isolated from living organisms and (ii) synthetic agents that are man-made by chemical synthesis. In the development of new antifouling agents, the EC50 value and the therapeutic ratio LC50/EC50 of an antifouling agent are commonly used to rate its antifouling activity and toxicity, respectively (Section 3.5).

#### 6.1. Natural agents

In recent years, the research focus has been shifted from the investigation of antifouling properties alone to a careful consideration of both the antifouling properties and environmental aspects. Therefore, in an attempt to find environmentally benign alternatives to toxic antifouling agents, researchers have isolated bioactive substances with antifouling properties from natural organisms such as terrestrial plants and marine organisms (Fig. 20) [111–113,326,327]. The chemical structures of the 21 active substances discussed in this section (hereinafter designates as Compound 7–27) derived from natural organisms is demonstrated in Fig. 21. All these substances belong to polycyclic compounds, including alkaloids, organic acids, lactones, terpenes, amides, etc. These compounds exhibit large structural diversity, ranging from simple monomeric molecules to more complex molecular scaffolds.

#### 6.1.1. Isolates from terrestrial plants

Extensive research has been done on natural antifoulants isolated from terrestrial plants such as chili pepper, the Campotheca acuminata tree or the black walnut tree, Nerium oleander, and others [328–332].

For example, Liu et al. [332] isolated four different cardenolides (a steroid type) from the plant *N. oleander*. These isolates were: odoroside A (Compound 7), digitoxigenin (Compound 8), oleandrin (Compound 9), and odoroside H (Compound 10). The corresponding chemical structures 7–10 are depicted in Fig. 21. These compounds displayed excellent inhibitory properties against barnacle settlement (EC50 values: 4.60, 32.09, 15.15, and 23.88 ng/mL, respectively). In addition, the evaluation against a non-target organism Artemia salina L. revealed moderate to low toxicity (LC50 values: 17.23, >100, 28.07, and 57.07 μg/mL respectively). Because *N. oleander* is widespread in many subtropical and tropical areas of the world and is easily collected, the natural antifoulants derived from *N. oleander* have potential advantages for large-scale applications.
6.1.2. Isolates from marine organisms

Marine organisms live in a complicated ocean environment and have to evolve antifouling mechanisms in order to adapt to such harsh conditions. Therefore, marine organisms provide a significant source for the isolation of natural antifoulants. Many marine organisms can keep their surfaces free from biofouling by generating secondary metabolites [333]. Natural antifoulants derived from these secondary metabolites can have excellent antifouling properties [334]. At the same time, as being already part of the ocean’s metabolic cycle, these substances are expected to be less harmful to the environment than synthetic substances that are not occurring naturally. For the above reasons, the secondary metabolites from marine organisms are regarded as promising candidates for antifouling agents. Table 3 shows an overview of the natural isolates which will be reviewed hereinafter.

For example, Nalini et al. [335] isolated a pyrrolo bioactive substance (Compound 11 in Fig. 21) from sponge-associated bacteria (Halobacillus kurosimensis SNSAB01). The substance displayed a significant effect against fouling organisms. Its minimum inhibitory concentration (MIC) against the bacteria Marinobacter sal_suginis CORC06 and Pseudoalteromonas flavipulchra CORAC03 was 125 μg/mL. Additionally, the pyrrolo substance inhibited 89% of the diatom (Amphora sp.) adhesion at a concentration of 350 μg/mL. The LC50/EC50 ratio of 3.0 (within the accepted target ratio > 1) indicated the nontoxic character of this substance via the mussel bioassay.

In their work, Shao et al. [336] isolated six different dihydroquinolin-2-one-containing alkaloids from the coral-derived fungus Scopulariopsis sp. which was collected in the South China Sea. The EC50 values attained with the dihydroquinoline derivatives (Compound 12 and 13 in Fig. 21) against barnacle B. amphitrite adhesion (17.5 pmol/L and 28 nmol/L respectively) implied higher antifouling activity compared to the value attained with the commercial antifoulant SeaNine 211™ (4.36 μmol/L). Additionally, Compound 12 and 13 had a higher therapeutic ratio (LC50/EC50: 1200 and 205, respectively) than the Sea-Nine 211™ (LC50/EC50: 20). In summary, Compound 12 and 13 were the most promising nontoxic anti-larval settlement candidates among the six dihydroquinoline derivatives.

The work of Zhang et al. [337] focused on subergonic acid (SA) (Compound 14 in Fig. 21) naturally occurring in a coral (Subergorgia suberosa) and additionally synthesized 26 subergonic acid derivatives of this acid. The inhibitory effect of these derivatives against the settlement of B. amphitrite was mainly attributed to the presence of double bond and ketone carbonyl functional groups. Furthermore, the introduction of benzyl esters improved the antifouling properties, while introducing a methylene chain into subergonic acid reduced the antifouling potency.

Wang et al. and Chen et al. investigated the suitability of indole-derivatives for antifouling applications [338–340]. Wang et al. [338] isolated eight natural products belonging to the di(1H-indol-3-yl)methane (DIM) family (Compound 15–22 in Fig. 21) from the bacterium Pseudovibrio denitrificans UST4–50 and evaluated their antifouling activity against the larval settlement of the barnacle B. amphitrite and the bryozoan Bugula neritina. All diindol-3-ylmethanes (DIMs) showed moderate to strong inhibitory effects against the larval settlement of B. amphitrite (EC50 values: 18.57–1.86 μmol/L). Compound 15 and 16 inhibited the settlement of larvae from the bryozoan B. neritina with EC50 values of 2.54 and 1.25 μmol/L, respectively. The structure-activity relationship of
DIMs suggested that the phenolic hydroxyl group enhanced the antifouling activity of DIMs. Furthermore, DIMs demonstrated comparable antifouling performance to the commercial antifouling biocide Sea-Nine 211™ in the field test for 5 months.

Wang et al. [339] isolated indole (Compound 23 in Fig. 21) and 3-formylindole (Compound 24 in Fig. 21) from a marine bacterium associated with the sea anemone Haliplanella sp. These two compounds inhibited byssal thread production of the green mussel Perna viridis significantly, with EC\textsubscript{50} values of 24.45 μg/mL for indole and 50.07 μg/mL for 3-formylindole. Additionally, the two substances exhibited antifouling activity against the barnacle Balanus albicostatus (EC\textsubscript{50} values of 8.84 and 0.43 μg/mL, respectively) and the marine bacterium Pseudomonas sp. (EC\textsubscript{50} values of 42.68 and 69.68 μg/mL, respectively).

Later on, Chen et al. [340] isolated indole alkaloids (Compound 25–27 in Fig. 21) from a gorgonian-derived fungus (Eurotium sp.) and evaluated their antifouling activities against the larval settlement of the barnacle B. amphitrite. Compound 26 and 27 inhibited the barnacle larval settlement with EC\textsubscript{50} values of 15.0 and 17.5 μg/mL, respectively, which were lower than the standard requirement of 25.0 mg/mL. Compound 25–27 showed low/nontoxic behavior to barnacle larvae with LC\textsubscript{50} > 50 μg/mL. EC\textsubscript{50} values

![Fig. 21. The molecule structures of natural antifouling agents.](image-url)
of the Compound 26 against coagulated eggs (48 h) and embryo death (72 h) were 20.8 and 9.9 μg/mL, respectively. However, Compound 26 displayed teratogenicity effects in zebrafish embryonic development, making it less suitable for the application as an antifouling. In contrast, the antifouling active Compounds 25 and 27 exhibited no teratogenicity effect on the zebrafish embryo.

In summary, even though most of the reported studies were conducted under laboratory conditions, natural antifoulants demonstrate a possibility of developing effective and, at the same time, nontoxic compounds for antifouling applications. Moreover, enhanced investigations into the mechanisms and structure-activity relationship of natural antifoulants will provide further insights for the targeted development of synthetic antifouling agents and novel antifouling approaches.

6.2. Synthetic agents

Although natural antifoulants show promising antifouling properties, their large-scale application is restricted due to the complexity of the separation and extraction processes. Therefore, scientists are trying to synthesize natural product analogues in a more facile and controllable production process. Additionally, by understanding the underlying structure-activity relationship, synthetic compounds with higher antifouling activity can be produced. For example, when Moubax et al. [341] compared natural bromoindole carbaldehydes with their synthetic derivatives, they found the synthetic compound to be more efficient than the natural one. The IC50 (half maximum inhibitory concentration) value on the cell division of sea urchin eggs of the synthetic 2, 5, 6-tribromoindole-3-carbaldehyde was much lower (0.31 μM/L) than that of the natural indole-3-carbaldehyde (40 μM/L) [341]. Fig. 22 shows the chemical structures of the 13 synthetic antifouling agents discussed in this section (hereinafter in the text as Compound 28–40). In a nutshell, the main task of research in this field is to develop synthetic antifouling substances that are as environmentally friendly and (even more) effective as their naturally occurring role models and, at the same time, applicable on a large scale. Natural substances which thereby typically serve as role models are: chalcone, capsaiacin, indole, or acids (e.g., amino or furoic acid).

6.2.1. The challenge to identify suitable substances

Faced with the vast multitude of bioactive compounds found in nature, the identification of suitable antifouling substances poses a real challenge. This issue is commonly encountered with a large number of trials. The quantitative effort of related studies is, for example, reflected in the paper published by Wang et al. [342]. They evaluated the antifouling activities and toxicities of 44 natural products isolated from marine invertebrates and symbiotic microorganisms and 11 modified compounds derived from these isolated products. Furthermore, in their review on molecular mechanisms of antifouling compounds, Chen et al. [110] propose future research to follow a workflow alternating between the testing of substances and the study of their structure-activity relationships. Such a workflow would allow for a progressively targeted identification and accelerate the development of suitable synthetic antifouling substances.

6.2.2. Synthetic agents derived from naturally occurring substances

Table 4 gives an overview of recently investigated synthetic antifouling agents and their characteristic values.

**Table 3** Overview of recently investigated natural antifouling agents, their natural sources, and characteristic values.

<table>
<thead>
<tr>
<th>Active substance</th>
<th>Natural source</th>
<th>Target species</th>
<th>Characteristic values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odoroside</td>
<td>Plant N. oleaner</td>
<td>Barnacle A. salina L.</td>
<td>EC50 = 4.60 ~ 23.88 ng/mL; LC50 = 17.23 ~ &gt;100 μg/mL; LC50/EC50 = 3.0</td>
<td>[332]</td>
</tr>
<tr>
<td>Pyrolo</td>
<td>Sponge-associated bacteria (H. kuroshimensis SNSAB01)</td>
<td>Bacteria (M. salsuginis CORCC06, P. flavipalcura CORAC03)</td>
<td>MIC = 125 μg/mL</td>
<td>[333]</td>
</tr>
<tr>
<td>Dihydroquinolin-2-one-containing alkaloid</td>
<td>Coral-derived fungus Scopulariopsis sp.</td>
<td>Barnacle B. amphitrite</td>
<td>EC50 = 17.5 μmol/L; 28 μmol/L; LC50/EC50 = 1200, 205</td>
<td>[336]</td>
</tr>
<tr>
<td>Subergonic acid</td>
<td>(1H-indol-3-yl)methane family</td>
<td>Coral (S. suberosa)</td>
<td>Barnacle B. amphitrite; bryozoa B. neritina</td>
<td>EC50 &gt; 25 μg/mL; LC50 &gt; 25 μg/mL; IC50 = 1.86 ~ 18.57 μmol/L; 1.25 ~ 2.54 μmol/L; LC50 &gt; 128.44 ~ &gt;326.65 μmol/L; &gt;147.87 ~ &gt;203.15 μmol/L</td>
</tr>
<tr>
<td>Indole, 3-formylindole</td>
<td>Bacterium associated with the sea anemone Halpianella sp.</td>
<td>Green mussel P. viridis, barnacle B. albicostatus, bacterium Pseudomonas sp.</td>
<td>EC50 = 24.45; 50.07 μg/mL; 8.84, 0.43 μg/mL; 42.68, 69.68 μg/mL</td>
<td>[339]</td>
</tr>
<tr>
<td>Indole alkaloid</td>
<td>Gorgonian-derived fungus (Eurotium sp.)</td>
<td>Barnacle B. amphitrite</td>
<td>EC50 = 15.0, 17.5 μg/mL; LC50 &gt; 50 μg/mL</td>
<td>[340]</td>
</tr>
</tbody>
</table>
Fig. 22. The molecule structures of synthesized antifouling agents.

Table 4
Overview of recently investigated synthetic antifouling agents and characteristic values.

<table>
<thead>
<tr>
<th>Active substances</th>
<th>Target species</th>
<th>Characteristic values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcone derivatives</td>
<td>Mussel larvae, <em>H. aquamarina</em>, <em>R. litoralis</em></td>
<td>EC$_{50}$ = 7.24, 16.48 μmol/L; 18.67, 18.78 μmol/L; 4.09, 12.34 μmol/L</td>
<td>[343]</td>
</tr>
<tr>
<td>Capsaicin derivatives</td>
<td><em>P. tricornutum</em>, <em>S. costatum</em>, <em>C. curvisetus</em></td>
<td>Inhibition rate: 95% (3 mg/L)</td>
<td>[344]</td>
</tr>
<tr>
<td>N-alkyl 2-furoates</td>
<td>Nauplii of the shrimp species <em>A. salina</em></td>
<td>LC$_{50}$ = 0.092, 0.454, 0.903 μg/mL</td>
<td>[345]</td>
</tr>
<tr>
<td>Isocyanides</td>
<td>Barnacles <em>B. amphitrite</em></td>
<td>EC$_{50}$ = 0.07 ~ 7.30 μg/mL</td>
<td>[346]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LC$<em>{50}$/EC$</em>{50}$ &gt; 1428.57</td>
<td></td>
</tr>
<tr>
<td>Acylamino compounds containing indole rings</td>
<td><em>E. coli</em>, <em>S. aureus</em></td>
<td>MIC = 0.03 ~ 0.06 mg/mL</td>
<td>[347]</td>
</tr>
<tr>
<td>Indole derivatives</td>
<td>Diatom <em>P. tricornutum</em>, <em>N. closterium</em>; <em>E. coli</em>, <em>S. aureus</em></td>
<td>Inhibition rate: &gt;90% (15 mg/L); &gt;80%, &gt;95% (30 mg/L)</td>
<td>[348]</td>
</tr>
<tr>
<td>7-hydroxy-4-methylcoumarin</td>
<td>Bivalve <em>Mytilus edulis platensis</em></td>
<td>EC$_{50}$ = 11 μg/cm$^2$</td>
<td>[349]</td>
</tr>
</tbody>
</table>
tives with fewer carbon atoms in the amide side chain exhibited a stronger inhibition effect against algae. Marine filed tests showed that only a few algae were attaching to the coatings incorporated with capsaicin derivatives after 90 days.

Furoate: Furoates are the salts or esters of furoic acid. Escobar et al. [345] evaluated the antifouling properties of three different n-alkyl 2-furatoates (Compounds 31–33 in Fig. 22). This was done by testing the antifouling activity against the nauplii of the shrimp species A. salina (LC50 values: 0.092 μg/mL, 0.454 μg/mL, and 0.903 μg/mL, respectively) as well as in field tests. A great reduction in settlement of fouling species (e.g., Hydrodium sp., Botryllus sp., and Polydora sp.) was detected on all three paints formulated with furoates. Among the three n-alkyl 2-furatoates, the compound with a shorter chain (butyl 2-furoate) (Compound 31) displayed the best performance compared to the others.

Isocyanide: Inoue et al. [346] synthesized 18 isocyanides derived from α,α-disubstituted amino acids and evaluated their antifouling activity/toxicity against the cypress larvae of B. amphitrite barnacles. Almost all derivatives showed superior antifouling properties (EC50 values: 0.07–7.30 μg/mL) without significant toxicity. With the highest antifouling activity (EC50 values: 0.07 μg/mL) and the maximum therapeutic ratio (> 1428.57), Compound 34 (Fig. 22) proved to be the most promising antifouling agent among isocyanide derivatives.

Indole: Indole is a widespread natural organic compound that can be produced by a multitude of bacteria. Indole derivatives isolated from the secondary metabolites of marine organisms not only show the excellent antifouling property but also possess advantages in terms of a relatively easy fabrication process and low toxicity [327,350–352]. For example, Feng et al. [347] synthesized two different acylimine compounds containing indole rings (Compounds 35 and 36 in Fig. 22). This was done via a Michael addition reaction and Mannich reaction, respectively. These compounds showed high antibacterial activity against E. coli and S. aureus which was expressed in MIC values in the range of 0.03–0.06 mg/mL. Additionally, practical panel tests were conducted in a marine environment and revealed that, compared to the control groups, fewer fouling organisms were found on the panels coated with the Compound 35 and 36 indicating antifouling activity. In a subsequently published work, Feng et al. [348] synthesized seven indole derivatives via the Friedel-Crafts alkylation reaction and tested the diatom and bacteria inhibition. The inhibition rate of Compound 37 (Fig. 22) against the diatom P. tricornutum and Compound 38 (Fig. 22) against the diatoms P. tricornutum and N. closterium was above 90%. Furthermore, antibacterial rates were measured: Among the seven indole derivatives, the antibacterial inhibition rates (E. coli and S. aureus) of Compound 37, 38, and 39 (Fig. 22) were above 80% and the rate for Compound 39 was even more than 95%. In a practical panel test under marine conditions, only a few biofilms appeared on the antifouling coatings incorporated with Compounds 38 and 39.

Currently, there is no consistent conclusion about the antifouling mechanism of indole derivatives. Among many proposed mechanisms, one generally accepted mechanism suggests that indole derivatives affect the cellular Ca2+ content. Nakahata et al. reported that indole derivative 5,6-dibromo-1,2-dimethylgramine evoked Ca2+ release from skeletal muscle sarcoplasmic reticulum through ryanodine receptors [353]. Iwata et al. revealed that 2,5,6-tribromo-1-methylgramine and 5,6-dibromo-1,2-dimethylgramine inhibited the smooth muscle contraction by inhibiting the Ca2+ entry [354]. With the development of measurement technology, a noninvasive micro-test technique came up which is now used to measure the concentration gradient of Ca2+ between two predetermined points. Yang et al. [355] reported that 6-chloroindole triggered the algal cellular Ca2+ efflux (Fig. 23a). The highest indole-triggered efflux value was 72.03 pmol/cm2/s, which was 10.6 times the value of the control group (Fig. 23b) [355]. Similar conclusions were made by Feng et al. [348] for Compound 37 (Fig. 22). Their Ca2+ efflux peak in algal cells under the influence of Compound 37 was nearly three times larger than that of the control group (Fig. 23c). It is generally known that calcium ions are related to the growth and development of organisms [356–358]. Therefore, the increase of Ca2+ efflux in the presence of indole derivatives is assumed to interrupt the Ca2+ balance of the cells and consequently inhibit the growth of the organisms. A schematic diagram of the antifouling mechanism of indole derivatives is shown in Fig. 23d.

6.2.3. Future trend: the application of green synthesis methods

In addition to the enhanced investigation of the structure-activity relationships of the antifouling substances, the application of so-called green chemistry techniques will become more and more important for the production of sustainable antifouling coatings. The advantages of green chemistry are the safer processes, reactants, techniques and products [349]. The use of toxic solvents and the formation of by-products is avoided by applying green synthesis technology [359]. This will be one of the best alternatives for traditional chemical synthesis methods while minimizing the waste of energy and reagents, and potential harm to the environment or personal safety [360]. In all, the essence of green chemistry can be summarized as follows [361]:

(i) Efficient utilization of raw materials, including the use of chemicals and energy resources in the synthesis process.
(ii) Reduction of the use of toxic or hazardous solvents and reagents.

For example, Pérez et al. [349] synthesized substances with antifouling activity by principles of green chemistry. They produced 7-hydroxy-4-methylcoumarin (Compound 40 in Fig. 22) and three n-alkyl 2-furatoates (Compounds 31–33 in Fig. 22). The antifouling activity of Compound 40 was evaluated in terms of the bivalve Mytilus edulis platensis under laboratory conditions. It effectively inhibited the settlement and byssogenesis of mussels (EC50 value of mussel attachment: 11 μg/cm2). In addition, coatings containing Compound 40 exhibited a significantly reduced fouling coverage after 90 days in practical marine panel tests.

While a large number of natural and synthetic antifouling agents are currently being developed, and published studies are showing encouraging results, there are still challenges that need to be addressed before these agents can be commercialized:

(i) The large-scale production at an affordable price,
(ii) A clear understanding of the antifouling mechanism,
(iii) The establishment of broad-spectrum antifouling laboratory tests and long-term sea immersion tests,
(iv) The evaluation of the long-term environmental effects.

To overcome these challenges, future antifouling studies need to be conducted in some sort of information feedback loop between the researchers producing synthetic agents and the ones studying the structure-activity relationships in naturally occurring substances, as was proposed in [110]. The chemists can draw lessons from the structure of natural bioactive compounds, and thereby further synthesize more efficient antifouling substances by chemical means. If the issues of mass production, broad-spectrum antifouling performance, and environmental friendliness are solved, natural antifouling agents and their derivatives will be promising potential to solve the worldwide antifouling problems.

7. Switchable coatings

Smart materials are attracting increased attention as components in marine coatings since they can increase the selectivity against fouling organisms and thereby environmental safety.
As they effectively switch their properties in response to external stimuli such as temperature, light, pH, and salinity [362], such coatings can trigger an on-demand activation of the biofouling control. Fig. 24 illustrates exemplary the basic working principles of some switchable antifouling and fouling-release coatings. From recent developments in medical applications and the food industry, it is known that switchable coatings can reduce protein and bacterial adhesion to surfaces [363–365]. Switchable coatings are not yet ready for application on a large scale. However, the investigation on their antifouling properties under marine conditions might become a growing trend because smart coatings can help to prevent the biofouling film formation from the start at its primary stage (Section 2).

7.1. pH-induced switching

Many of the currently used biocide-containing coatings can lose their antifouling properties in a short time due to a poorly controlled release of biocides. In terms of long-term performance and environmental safety, better control of biocide release represents a major research goal. pH-responsive materials are well known in the field of drug delivery systems in pharmaceutical research [366]. This property, i.e. the pH-responsive release of drugs, can also be exploited when developing new marine antifouling coatings [367,368]. Metabolic byproducts produced by organisms, such as secretions produced by bacteria, can alter the pH value of their surrounding [369]. In this case, a pH-responsive antifouling coating, which is otherwise inactive, could switch its properties and start releasing biocides, as soon as bacteria attached to the ship hull.

Usually, the pH-response takes place at the surface of biocide-loaded capsules, which in turn triggers the on-demand biocide release by some sort of chain reaction:

(i) The bacterial metabolism produces an acidic environment.
(ii) The drop in pH value changes the polarity of an amine-rich surface.
(iii) The encapsulating material swells or is biodegraded.
(iv) The encapsulating material releases biocides.

For example, Wang et al. [369] used the natural-based and biodegradable polymer chitosan as pH-responsive encapsulation material. The capsainc@chitosan nanocapsules were prepared by a micro-emulsion approach. As the dissociation constant (pKₐ) of chitosan is around 6.5, the nanocapsules will swell due to the protonation of amino groups and release embedded biocides when the environmental pH is lower than 6.5 (i.e., acidic condition) [370]. The pH value of seawater is typically basic (pH 7.5–8.4) [371]. Due to the bacterial attachment and reproduction on the material surfaces, the local environment was acidified which triggered the expansion of chitosan and thus the release of capsainc (Fig. 25a). Fig. 25b shows a schematic sketch illustrating the biocide release mechanism.
Su et al. [372] used another approach to prepare a pH-responsive biocide encapsulation and prepared self-assembled micelle carriers. They used a copolymer based on polyurethane (PU) and containing biodegradable polycaprolactone (PCL) and poly(ethylene glycol) (PEG). In water, this co-polymer self-assembled into micelles with a PCL core and a PEG corona due to the hydrophobic and hydrophilic character of the PCL and PEG, respectively. Different types of micelles were synthesized by attaching the PEG onto the PU chains at different locations. One of the micelle types carried the tertiary amine groups from the PEG at the surface and showed a pH-dependent switching of the surface charge. Triclosan was injected into the biodegradable PCL core of the different types of micelles. The micelles could switch their surface state in an acidic environment, and the micelle which exposed the PEG at its surface, performed the best as antifoulant. The model describes a multistep mechanism and can be summarized as follows: (i) The micelles surface was charged in the acidic environment; (ii) The micelles got attracted electrostatically to the biofilm. (iii) They were degraded by metabolic byproducts of the organisms and incorporated into the film. (iv) They thus started the triclosan release.

Another possibility to exploit the pH-responsiveness of amine groups is to develop coatings with switchable wettability. As shown in previous studies [373], poly (dimethylamino) ethyl methacrylate (PDMAEMA) and its derivatives can respond to changes in the pH value due to the protonation/deprotonation of its tertiary amine groups (Fig. 25c). Fu et al. [376] fabricated antibacterial fabrics with pH-responsive wettability by using quaternary ammonium salts-functionalized fluorinated copolymer containing PDMAEMA segments. The N+ concentration of the surface significantly increased under an acidic environment, resulting in a rapid wettability conversion from superhydrophobicity to superhydrophilicity.

Besides working on switchable surface groups, researchers also developed coatings that switch on the basis of internal pH-responsive linkages. pH-sensitive linkages (e.g., imine) undergo cleavage at an acidic condition (typical pH 5.0–6.5) and are stable when the pH is slightly above neutral. For example, Xu et al. [371] fabricated a pH-responsive self-polishing coating (Section 5.1). It is based on pH-cleavable linkages of two kinds of polysaccharides (i.e., dextran and chitosan). Dextran aldehyde and carboxymethyl chitosan were synthesized and alternately incorporated via imine linkage into a multilayer coating fabricated in a layer-by-layer deposition process (Fig. 25d). It was shown that acidification occurred when a dense bacterial attachment was established which in turn induced the detachment of the outmost layer of the coating, thus at the same time, the release of the attached biofouling (Fig. 25e).

### 7.2. Temperature-induced switching

Temperature is one of the most common stimuli that has been widely used to control bio-adhesion on surfaces [377–379]. Poly(N-isopropylacrylamide) (PNIPAM) is a typical thermo-responsive polymer that exhibits reversible changes in water solubility in response to temperature changes across a lower critical solution temperature of 32 °C in an aqueous solution [380]. The lower critical solution temperature represents the common minima of the spinodal and coexistence curves in the polymer-water mixture where a transition from a stable one-phase to an unstable two-phase system occurs with the increase of system temperature [382]. This temperature-induced hydrophilic/hydrophobic (swelling/shrinking) transition is reversible as the polymer solution can regenerate the initial state by lowering the temperature [362]. Due to its temperature-responsive wettability, PNIPAM-modified surfaces were found to possess promising fouling-release properties in terms of cells and bacteria adhesion [381,382].

Recently, Li et al. [374] found that thermo-responsive, dynamic polymer brushes made from PNIPAM can be used to control the release of dead bacteria from a surface submerged in water. In their study, the PNIPAM-grafted polymer surface was synthesized by radical cation-initiated polymerization. The grafting reaction took place on iodine (I2) doped and darkened rubber of trans-polyisoprene (TPI). The ability of the darkened TPI rubber to heat up by photothermal conversion induced changes in the antifouling and fouling-release properties of the coating: First, a release of iodine could be realized via light irradiation, leading to the death of bacteria. Second, the increased temperature triggered the solubility of PNIPAM to switch from the hydrated (elongated chains) into the dehydrated (shrunken chains) state. When cooled again, the polymer chains re-elongated which promoted the release of the dead bacteria (Fig. 25f).

### 7.3. Light-induced switching

Among the available external stimuli, light has advantages as it can be delivered to the surface from a remote source [383]. Using
Fig. 25. Examples of switchable biofouling control coatings. a) Cumulative release percentage of capsaicin under alternate cycling test. b) The mechanism of the pH-responsive releasing of capsaicin@chitosan nanocapsules [369]. Copyright 2018. Adapted with permission from Elsevier. c) Reversible surface wettability changes of block copolymer PHFBMA-b-PDMAEMA at different pH driven by the protonation/deprotonation of tertiary amine groups [371]. Copyright 2016. Adapted with permission from John Wiley and Sons. d) Preparation of pH-responsive self-polishing coating based on cleavable linkages of two kinds of polysaccharides (i.e., dextran and chitosan) via layer-by-layer deposition. e) Self-polishing mechanism of the coating based on pH-cleavable linkages [371]. Copyright 2018. Adapted with permission from the American Chemical Society. f) Scheme showing the interaction between different TPI slices and bacteria at different temperatures [374]. Copyright 2018. Adapted with permission from John Wiley and Sons. g) Photocatalytic mechanism of the prepared spherical TiO₂/silicone nanocomposites under UV light [375]. Copyright 2016. Adapted with permission from Elsevier.
light as a trigger usually does not influence the local environment or cause unwanted side effects [384,385].

In the past decades, TiO₂ has gained considerable attention as it offers excellent photo-activity, high physical and chemical stability, low cost, easy availability, and low toxicity [386]. The photocatalytic cleaning and anti-bacterial effect of TiO₂ containing surfaces have been widely reported [387–389]. The antifouling effect of TiO₂ is mostly due to the reactive oxygen species generated under illumination [387]. Moreover, TiO₂ is well known to have UV light-responsive wettability [390–392].

TiO₂ has been tested as an ingredient of different biofouling control coatings. For example, Selim et al. [375] synthesized rutile TiO₂ nanoparticles with dominant [110] facets using a sol-gel technique. The particles were incorporated into a PDMS matrix. It was shown that the TiO₂ nanoparticles significantly influenced the surface morphology, superhydrophilicity, and self-cleaning efficiency of the coating upon irradiation with pulsed UV (Fig. 25g). The TiO₂ modified PDMS coating demonstrated good fouling resistance towards micro- and macrofouling organisms throughout 365 days of exposure in the Suez Canal, Egypt. Other than Selim et al. [375], Natarajan et al. [393] used a coating matrix based on chitosan. They showed that the incorporation of TiO₂ and Ag nanoparticles improved the antifouling performance against marine algae Dunaliella salina under UV exposure due to the enhanced photocatalytic effect of TiO₂ with Ag nanoparticles.

In a nutshell, a lot of research has been done on the switching mechanisms of smart surfaces including surfaces responsive not only to pH, temperature, and light but also to solvents, salt concentration, and CO₂ capture [394–396]. However, most of the research on smart surfaces is towards antibacterial properties commonly needed in medical application. For example, the smart anti-bacterial surfaces based on the ‘kill-release’ strategy have undergone rapid development in the last few years. Those surfaces can kill the attached bacteria and then release the dead bacteria under an appropriate stimulus, thereby maintaining long-term effective antibacterial activity [383]. In the case of marine antifouling application, further investigations are needed including the selection of suitable stimuli, fabrication process, and field tests.

8. Biomimetic coatings

In nature, numerous organisms exhibit excellent antifouling performance, especially those from the marine environment (e.g., sharks, whales, etc.) [397,398]. Due to the current trend towards the development of environmentally friendly coatings, more and more researchers have been trying to imitate the surface properties of different plant and animal species. The two key strategies for biofouling prevention that researchers have learned from nature and applied to artificial surfaces are:

(i) The imitation of physicochemical surface properties of plants and aquatic animals [220,395],

(ii) The extraction of active substances from organisms (e.g., secondary metabolites) for the use as an antifouling agent (Section 6) [399].

Researchers have been developing biomimetic surfaces based on different natural skins. Here, the sharkskin is an excellent example of a biological surface, where the surface texture plays a crucial role in reducing the settlement of marine organisms. More specifically, the biofouling preventing performance has been attributed to the microstructured riblets, flexion of dermal denticles, and a mucous layer of the surface [400,401]. Fabrication of surfaces with a sharkskin-like structure has become a hot research topic in the field of biomimetic biofouling preventing coatings [402–404]. However, surface microstructure alone may not be sufficient to obtain long-term biofouling control under realistic conditions. Investigations of defense mechanisms of different marine organisms led researchers to the conclusion that the combination of topography and chemical composition of the surface is essential to obtain the desired surface properties [405].

8.1. Surfaces inspired by sharkskin

Recently, Dunbar Arisoy et al. [406] developed a multifunctional surface (Fig. 26a) that works on the basis of a patterned polymeric surface combined with chemically active nanoparticles. This surface can decrease the microbial attachment and inactive attached microorganisms due to a combination of the sharkskin-like microstructure with antibacterial titanium dioxide (TiO₂) nanoparticles. A UV-crosslinkable adhesive (Norland Optical Adhesive) was mixed with TiO₂ nanoparticles and applied on a poly(ethylene terephthalate) substrate. The sharkskin microstructures were imprinted through solvent-assisted soft nanoimprint lithography on poly(ethylene terephthalate) substrates. The fabricated surface reduced the attachment of E. coli by ~70% compared to a smooth surface with the same chemical composition. After the incorporation of 10 wt% TiO₂ into the sharkskin-patterned surface, over 95% E. coli and up to 80% S. aureus were inactivated within 1 h UV light exposure.

Likewise, Qin et al. [178] added inorganic nanoparticles to a patterned polymeric surface, but in this case, the particles were only used for texturing. They prepared dual bioinspired sharkskin and lotus structure (Fig. 26b) on a PU surface by a two-step process comprising microcasting and nanosphere spraying. After a dehydration treatment, the soft tissue under the rigid original sharkskin was used as the sharkskin template for replication. First, the sharkskin pattern was transferred onto PU by a vacuum casting procedure by using a negative silicone mold fabricated from the sharkskin. In the second step, mesoporous silica nanospheres were sprayed onto the structured PU surface to create a lotus-like nano-feature. The water contact angle of the dual-treated surfaces increased by 29° compared to the unsprayed surfaces, and the shear stress measurements revealed a reduction of the fluid drag by 36.7%. The contaminant mass on the structured surface was reduced by 76% compared to the flat PU polymer by measuring the residual mass of the pollutants after washing. Yang et al. [407], however, used an approach free from additional nanoparticles but including chemically active side groups instead. They fabricated sharkskin-inspired surfaces (Fig. 26c) with different feature heights and introduced chemical moieties (hydroxyl groups and methyl end groups) on the surface via O₂ plasma treatment and immersion in a n-dodecyltrimethoxysilane solution. The modified surfaces showed promising results in the protein adsorption assay. It was suggested that the chemical modification inhibited the protein adsorption while the micropatterning contributed to the removal of the unstable adsorbate through the self-cleaning process.

Since the denticles on natural sharkskin are not of constant height, Munther et al. [408] integrated an additional height gradient into the patterned surface. They prepared plasoid scale patterns with an engineered height gradient on the PDMS surface by means of a micro-molding technique using etched silicon molds (Fig. 26d). The E. coli settlement on the biomimetic surfaces was reduced by 75% compared with the completely featureless control surface.

8.2. Surfaces inspired by non-marine organisms

Besides marine organisms, many other structures found in nature’s flora and fauna also show excellent antifouling performance [411]. For example, Xiao et al. [92] decorated the surface of PDMS with a honeycomb-like microstructure, which significantly reduced
the density of diatom *N. incerta* compared to a smooth PDMS surface.

In contrast, the work of Ware et al. [164] was inspired by pitcher plants. These plants use their microstructure to retain an intermediary liquid and form a thin oil-repellent slippery surface. They prepared a nanostructured wrinkled surface by applying a rigid polymer layer (Teflon) on top of a shrinkable polyethylene substrate (Fig. 26e). Thereby silicone oil was infused into the wrinkled surface to mimic the pitcher plant’s lubricating mechanism. The bacterial attachment test showed that the wrinkled surface’s inhibitory rate with 0.9 μL/cm² silicone oil against *Pseudoalteromonas* spp. was up to 99%.

In addition to imitating and adapting biological solutions for artificial surfaces, researchers also attempted to accurately copy the microscopic morphology of some natural organisms through a series of material replication steps. The fabrication of such surfaces can be roughly divided into two main steps: (i) Polymer A is used as a negative mold to replicate the biological sample surface, and (ii) polymer B is cast into the mold to give the surface the desired morphology. For example, Chen et al. [409] prepared siloxane-modified acrylic resin coatings with a texture replicating the surface of a lotus leaf (Fig. 26f), resulting in attachment reduction of *Closterium* and *Navicula* by more than 70% compared to a smooth coating. This effect was attributed to a combination of the specific micro-/nanostructures and the low surface energy of the material.

Furthermore, inspired by the superior biofouling control performance of the *Sonneratia apetala* mangrove tree leaves, Fu et al. [410] prepared PDMS surfaces with the microscopic ridge-like morphology (Fig. 26g). The samples were placed into a petri dish containing seawater and tubeworms. After 24 h immersion, the number of tubeworms settled on the microstructured PDMS was less than 5% of that on the smooth PDMS surface.

Encouraging results were also obtained by Gangadoo et al. [177], who replicated the pattern of superhydrophobic cicada *Psaltoda claripennis* wings on the epoxy resin (Fig. 26h). The protein adsorption on the replicated sample was reduced by 48% compared to the smooth epoxy resin sample.

In summary, in recent years, researchers have made great progress in the fabrication of biomimetic surfaces providing alternative environmentally friendly approaches for biofouling control. Nevertheless, although the efficiency of bioinspired surfaces against specific biofouling species was shown to be successful under laboratory conditions, the performance of such surfaces under complex marine environmental conditions still needs to be proven [412]. Furthermore, upscaling of the fabrication technology to large-scale applications as well as production costs need to be kept in mind.

9. Additional antifouling and cleaning strategies

In addition to the biofouling control coatings applied on the ship’s hull, mechanical removal of the biofouling by an underwater hull cleaning may be necessary if the hull surface is heavily fouled.
### Table 5
Recently developed biofouling control coatings and technologies, with working principle, strength, and weakness.

<table>
<thead>
<tr>
<th>Approaches</th>
<th>Working principle, Materials &amp; Technologies</th>
<th>Strength</th>
<th>Weakness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coatings based on wettability</td>
<td>(Super-)hydrophobic: <em>low surface energy, micro-/nanoroughness</em>; <em>PDMS, fluoropolymer</em>; <em>inclusion of micro-/nanoparticles</em>; <em>formation of the hydration layer</em>; <em>PEG, acrylate, zwitterionic polymer</em>; <em>polymer brushes and hydrogels</em>; <em>&quot;grafting to&quot; and &quot;graft from&quot;</em> approaches</td>
<td>+ good fouling-release (macrofouling); + available on the market; + high protein absorption resistance</td>
<td>- limited antifouling (microfouling); - shear force required; - week mechanical, substrate adhesion strength; - relatively high cost; - poor fouling-release under real marine conditions; - poor mechanical properties; - limited stability; - limited large-scale fabrication of zwitterionic polymers</td>
</tr>
<tr>
<td></td>
<td>(Super-)hydrophilic: <em>introduction of polar or ionic groups</em>; <em>PEG, acrylate, zwitterionic polymer</em>; <em>polymer brushes and hydrogels</em>; <em>&quot;grafting to&quot; and &quot;graft from&quot;</em> approaches</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphiphilic</td>
<td><em>coexistence of hydrophobic and hydrophilic domains on a nanoscale</em>; <em>PDMS, fluoropolymer, PEG</em></td>
<td>+ high resistance to a wide variety of organisms under laboratory conditions</td>
<td>- more studies needed under real marine conditions; - limited large-scale fabrication; - high cost; - shear force required for the self-polishing process; - release of metals (e.g., Zn and Cu) monomers; - accumulation of microplastics; - high cost of silicon hydrolyzable polymers</td>
</tr>
<tr>
<td>Self-renewable coatings</td>
<td>Self-polishing: <em>side chain hydrolyzation</em>; <em>can be used as antifouulant carriers</em>; <em>acrylate-based copolymers</em>; <em>zinc, copper, silicon, and boron groups as hydrolyzable side chains</em></td>
<td>+ good anti-fouling under dynamic conditions; + available on the market</td>
<td>- use of toxic adjuvants during synthesis under development; - polymer matrix dependency of the release rate; - complex extraction process; - limited large-scale fabrication</td>
</tr>
<tr>
<td>Degradable</td>
<td><em>size chain hydrolyzation and main chain degradation</em>; <em>can be used as antifouulant carriers</em>; <em>polyester polyurethane, acrylate</em></td>
<td>+ good anti-fouling under static condition</td>
<td>- polymer matrix dependency of the release rate; - environmental impact unknown; - limited or no experience under real marine conditions; - limited large-scale fabrication; - limited control of stimuli under real marine conditions</td>
</tr>
<tr>
<td>Coatings containing antifoulants</td>
<td>Natural agents: <em>natural anti-fouling activity</em>; <em>alkaloids, organic acids, lactones, terpenes, amides, etc.</em>; <em>isolated from terrestrial plants &amp; secondary metabolites of marine organisms</em></td>
<td>+ good anti-fouling; + environmentally friendly</td>
<td>- antifouling mechanism not completely clear; - polymer matrix dependency of the release rate; - environmental impact unknown; - limited or no experience under real marine conditions; - limited large-scale fabrication; - limited control of stimuli under real marine conditions</td>
</tr>
<tr>
<td></td>
<td>Synthetic agents: <em>synthetic analogs to natural agents</em>; <em>alkaloids, organic acids, lactones, terpenes, amides, etc.</em></td>
<td>+ good anti-fouling; + available on the market (e.g., Sea-Nine 211™)</td>
<td>- antifouling mechanism not completely clear; - polymer matrix dependency of the release rate; - environmental impact unknown; - limited or no experience under real marine conditions; - limited large-scale fabrication; - limited control of stimuli under real marine conditions</td>
</tr>
<tr>
<td>Switchable coatings</td>
<td><em>stimuli: pH, temperature, light, etc.</em>; <em>controlled biocides release, e.g., chitosan</em>; <em>polymer brushes movement, e.g., PNIAM</em>; <em>linkage cleavage, e.g., imine groups</em></td>
<td>+ good anti-fouling under laboratory conditions (proteins, bacteria)</td>
<td>- antifouling mechanism not completely clear; - polymer matrix dependency of the release rate; - environmental impact unknown; - limited or no experience under real marine conditions; - limited large-scale fabrication; - limited control of stimuli under real marine conditions</td>
</tr>
<tr>
<td>Biomimetic coatings</td>
<td><em>imitation of physicochemical surface properties of plants and aquatic animals (e.g., sharkskin)</em>; <em>micro/nanoroughness</em>; <em>UV photolithography, nanoimprint lithography, etching.</em></td>
<td>+ good anti-fouling under laboratory conditions</td>
<td>- antifouling mechanism not completely clear; - polymer matrix dependency of the release rate; - environmental impact unknown; - limited or no experience under real marine conditions; - limited large-scale fabrication; - limited control of stimuli under real marine conditions</td>
</tr>
<tr>
<td>Additional strategies</td>
<td><em>biomimetic replication technique</em>; <em>mechanical cleaning, ultrasonic system, UV irradiation, etc.</em></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Summarized by Song and Cui [413], the cleaning approaches can be classified into three categories:

(i) manual hull cleaning,
(ii) powered rotary brush cleaning systems,
(iii) non-contact cleaning technology (e.g., high-pressure water jet, cavitation water jet, ultrasonic cleaning, etc.).

Moreover, regular underwater hull cleaning (grooming) has been shown to be efficient to avoid the build-up of biofouling [414,415]. However, the hull cleaning procedure can easily destroy the coating surface and remove the biocides from most of the commercially used coatings. Thus, to realize this approach in the long term, the coating should be mechanically stable against abrasion and contain no biocides. Furthermore, as hull cleaning does not kill all the removed organisms, underwater cleaning of foreign vessels in the port or territorial areas is prohibited by laws in some countries and regions to avoid the introduction of neobiota [413]. Thus, underwater cleaning systems are usually equipped with pipes and suction devices.

In addition to mechanical cleaning, alternative approaches such as ultrasound systems, ultraviolet irradiation, and storage out of seawater are investigated as well since they are supposed to create physically and chemically unfavorable conditions for the organism’s attachment. However, less information is available about the environmental impact of these approaches under water. Moreover, their application can be limited in terms of complicated marine conditions and implementation, and is restricted by the regulations in different countries and regions [413,416].

### 10. Summary and outlook

Previously widespread TBT-containing coatings caused serious harm to non-target organisms, such as severe shell deformations, growth impediments, and reproductive failure in oyster cultures.
The commercial alternatives containing biocides are less toxic compared to TBT-containing coatings, but still have negative effects on the ecosystem “Ocean”. Therefore, the need for environmentally benign, alternative biofouling control coatings is strong, and the research in this field is growing rapidly. Table 5 summarizes the key points (working principle, materials and technologies used, biofouling control performance, cost, and industrial applicability) of the recently developed coatings reviewed in this article.

Currently, the hydrophobic fouling-release coatings (e.g., PDMS-based coatings) and the self-polishing coatings (e.g., zinc acrylate copolymers) are commercially available. However, these coatings have deficiencies under static conditions since a certain shear force (e.g., present during a ship moving) is required to achieve an optimal biofouling control performance. Biocides are commonly incorporated into such coatings to improve the antifouling properties, which are, in turn, unfriendly to the environment. Moreover, the non-degradable main chain of the self-polishing coatings can lead to an accumulation of the microplastics. This can be solved by the recently developed degradable coatings, which are not only hydrolyzable in the side chain but also degradable in the main chain. As more biofriendly natural antifouling agents and synthetic antifouling agents derived from nature have been discovered recently, a combination of the more biofriendly antifouling agents with the fouling-release or degradable coatings can be a development trend in the future. However, extraction of the natural antifouling agents on an industrial scale and production of degradable coatings and synthetic antifouling agents in a sustainable process (e.g., using nontoxic solvents and forming non-harmful by-products) need to be achieved in the future. As for the development trend of fouling-release coatings, besides adding biofriendly antifouling agents, the surface physiochemical properties can be modified to achieve better biofouling control properties by, e.g., the addition of amphiphilic moieties, fabrication of biomimetic structures, and switchable surfaces. However, the problems of high cost and limited fabrication scale of such approaches should be solved in the future. Furthermore, most biofouling control tests of such surfaces are only conducted in the laboratory, especially for switchable coatings. This is due to the complex marine condition and the uncontrollable stimuli in the ocean. Thus, the development of a switchable coating that can respond to multi stimuli as well as manually introducing the stimuli (e.g., UV light) to the surface may be necessary in the future. Faster and more sensitive responses in switching properties (e.g., change in surface wettability, controlled release of natural antifouling agents, and controlled degradation of the coatings) need to be further developed. As high mechanical strength and good adhesion-to-substrate are always required for marine coatings to withstand the harsh marine conditions, fabrication of polymer composites from highly stable materials like polyethyleneurethane (PTU) and incorporation of special-shaped micro-/nanoparticles like tetrapodal ZnO into the biofouling control coatings for mechanical reinforcement can be a promising approach.

Overall, there is still much work to be done to develop long-term effective and environmentally friendly biofouling control coatings or technologies. In the future, the development should be focused on the fabrication of synergetic coatings with the biofouling control properties from different strategies. However, the multiple factors (e.g., environmental friendliness, cost-effectiveness, large-scale production, and universality in different marine conditions) should always be kept in mind in future development. We hope that the completeness of this review, as well as its clear focus on marine applications, will prompt scientists and engineers in the fields of materials science, physics, chemistry, biology, and other multidisciplinary research fields to develop environmentally friendly and efficient biofouling control coatings and technologies for the sustainable marine industry.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was funded by the Federal Ministry for Economic Affairs and Energy within the ZIM-program (16KN021267, 16KN078723), and the Cluster of Excellence 80 “The Future Ocean.” The “Future Ocean” is funded within the framework of the Excellence Initiative by the Deutsche Forschungsgemeinschaft (DFG) on behalf of the German federal and state governments. Dr. Kang Feng acknowledges financial support from the China Scholarship Council (Fellowship Award). YKM acknowledges funding by Interreg Deutschland-Denmark with money from the European Regional Development Fund, project number 096-11-18.

References

Contreras-Naranjo 1977;14:285–443

Maki 2016.

protein of native  

Bressy coatings. 


Höllert L. Mechanically stable and environmentally friendly polymer/composite systems for the application as low-fouling coating in the marine sector. 2016.


Harder T, Yee LH. Bacterial adhesion and marine fouling. Woodhead Publishing Limited; 2009.


Maki 2016.


Wagemann M. Adhesion in blue mussels (Mytilus edulis) and barnacles (Genus Balanus): mechanisms and technical applications. Aquat Sci 2005;67:166–76.


nanometer approach. ACS Chem. N”2017;147:064703


Schmidt DI, Brady RF, Lam K, Schmidt DC, Chaudhry MK. Contact angle hysteresis: a thermodynamic and fuel release–adhesion. ACS Appl Mater Interfaces 2004;208:2830–6. 1


Wu CJ, Li YF, Woon WY, Sheng YJ, Tsao HK. Contact angle hysteresis on...


[38] Miller J, Driessche CT, OW, Paul DR. Jenkens BD. Surface modification of water purification membranes. Angew Chemie - Int Ed 2017;56:4662–711.


Zhou and Chen, S. N. M. A. Polyelectrolyte brushes.


H. Qiu, K. Feng, A. Gapeeva et al.  
Progress in Polymer Science 127 (2022) 101516


