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Polymers for anti-fouling applications: a review

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Marine fouling is the buildup of unwanted organisms on submerged surfaces, and it creates major challenges for industries such as shipping, aquaculture, and marine infrastructure. Traditional anti-fouling coatings often rely on toxic biocides, which raise many environmental and regulatory concerns. To address this, researchers have been exploring polymer-based materials as a more sustainable alternative. This review examines their effectiveness through a series of laboratory and real-world tests, including static immersion and dynamic exposure trials in marine environments. The findings show that polymer-based coatings significantly reduce bio-fouling by preventing the attachment of marine organisms, leading to lower maintenance costs and improved efficiency for vessels and marine structures. While synthetic polymers are not highly biodegradable, this can actually be an advantage in maintaining long-term anti-fouling performance. Looking ahead, future research should focus on enhancing the eco-friendliness of these materials by incorporating biodegradable or bioinspired polymers, optimizing surface properties, and developing multifunctional coatings. By providing a viable alternative to toxic biocides, polymer-based anti-fouling materials offer a promising step toward cleaner, more sustainable oceans.

Environmental significance

The use of polymers in anti-fouling applications presents a sustainable and environmentally friendly alternative to traditional antifouling coatings, which often rely on toxic biocides and heavy metals. Polymer-based coatings can be designed to prevent biofouling through non-toxic mechanisms such as surface modification, hydration layers, or controlled-release strategies, which significantly reduce the ecological impact on marine ecosystems. These advanced materials contribute to improving fuel efficiency, reducing greenhouse gas emissions from marine vessels, and extending the lifespan of submerged structures. By minimizing the release of harmful substances into aquatic environments, polymer-based antifouling technologies support cleaner waterways and promote long-term ecological balance.

1. Introduction

The concept of preventing fouling in marine applications may have been initially developed in 300 BC when sheets of heavy metal were used to cover wooden boats. The metal sheets were used as an anti-fouling substance to reduce the formation of bio-fouling on the wood surface of the boats. Anti-fouling materials are designed to prevent or reduce the formation of bio-fouling species on surfaces. Bio-fouling is an undesirable phenomena, and occurs when microorganisms, plants, and marine animals congregate and colonize on wetted material surfaces, including ships, sea-farming devices, and power-plant cooling tubes.

The first step in microbial bio-fouling is the formation of a molecular conditioning film. After that, biofilm will be formed by the attachment of single-celled organisms, such as bacteria and algae. This step is followed by the formation of macro-fouling as a result of the attachment of higher multicellular organisms, such as barnacles. Fig. 1 illustrates the steps that occur in bio-fouling formation.[1] A full understanding of these steps is important for the researcher so that the correct anti-fouling solutions can be developed for each particular environment. The occurrence of bio-fouling results in rough ship surfaces, which increases fuel consumption, corrosion, and dry-docking cleaning frequency, and also leads to the loss of speed and potential invasion of alien aquatic species. Therefore, to prevent or reduce these effects, anti-fouling coatings are used.

Anti-fouling materials may be toxic, such as copper, which is widely used to provide effective control of many bio-fouling species. Due to environmental concerns, non-toxic anti-fouling materials based on polymer hydrogels have been designed. A cross-linked polyethylene glycol (PEG)-based hydrogel was synthesized by H. Ju and his colleagues using PEG diacrylate as a cross-linker and PEG acrylate, 2-hydroxyethelacrylate, or acrylic acid co-monomers. This anti-fouling substance was prepared to reduce membrane fouling in water

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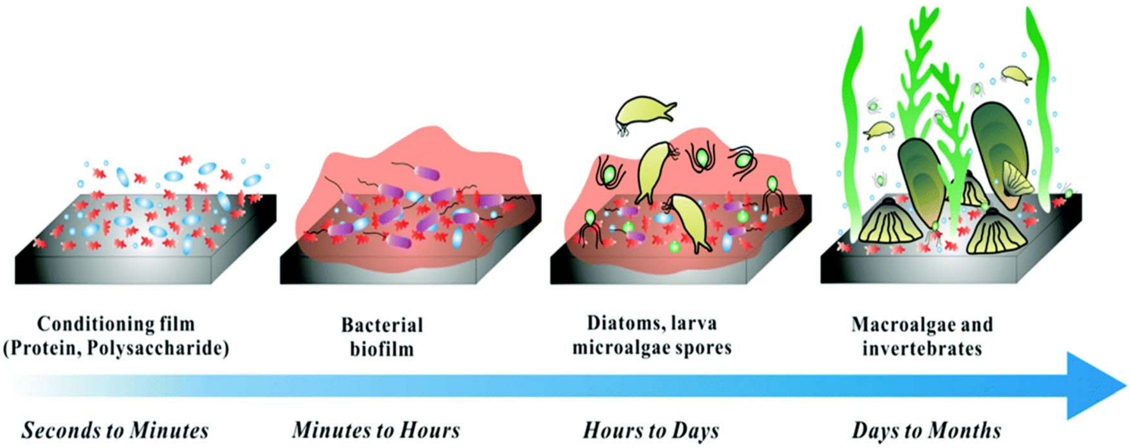

Fig. 1 The steps in the process of bio-fouling.[1]

purification applications.[2] In another study by Wallström *et al.*, prototype paint was prepared using silica gel, a binder system, and filler pigments. The effects of zinc pyrithione on biocide release and gel properties on water uptake were investigated.[3] According to previous research, various chemical, physical, and mechanical properties of anti-fouling-based polymers need to be taken into consideration if they are to be used in marine applications as bio-fouling protectors. Chemical, thermal, and pH stability are important properties of anti-fouling materials that significantly affect their interactions with biological environments. The need for a deep understanding of anti-fouling hydrogel materials in terms of properties and working mechanisms is the main objective of this review.

2. Raw materials for anti-fouling applications

Anti-fouling coatings can be formulated using a variety of raw materials, each contributing specific properties to the final coating. These raw materials are selected based on factors such as their ability to prevent fouling, durability, environmental impact, and regulatory compliance. The raw materials used to formulate anti-fouling coatings are:

(i) Biocidal compounds: these are chemicals that kill or inhibit the growth of fouling organisms such as algae, barnacles, and mollusks. Common biocides used in anti-fouling are copper compounds (*e.g.*, copper oxide, copper pyrithione), organotin compounds (*e.g.*, tributyltin, triphenyltin), zinc pyrithion, and Irgarol.[4–6]

(ii) Polymers: used as binders or matrix materials in anti-fouling coatings to hold other ingredients together and provide adhesion to the substrate. Examples of polymers used in anti-fouling coatings are silicone polymers, fluoropolymers (*e.g.*, polytetrafluoroethylene, perfluoroalkoxy), polyurethanes, acrylic polymers, and polysiloxane copolymers.[7–11]

(iii) Hydrophobic agents: these are substances that repel water and create a non-wettable surface, to which it will be difficult for fouling organisms to attach. Common hydrophobic agents used in anti-fouling coatings are silicone oils, fluorinated compounds (*e.g.*, perfluorooctane, perfluoropolyethers), and polyethylene glycol (PEG) derivatives.[12–16]

(iv) Fouling-release additives: these additives are substances that modify the surface properties of coatings to prevent fouling organisms from adhering. Examples of fouling-release additives are silicone elastomer, hydrogel polymers, polysiloxane copolymers, and polyurethane acrylate.[17–24]

(v) Fillers and reinforcements: fillers and reinforcements are added to anti-fouling coatings to improve mechanical properties, enhance durability, and reduce cost. Common fillers and reinforcements used in anti-fouling coatings are silica, calcium carbonate, glass microspheres, carbon black, and glass fibers.[25–30]

(vi) Solvents: solvents and carriers are used to dissolve or disperse other ingredients in a coating formulation and facilitate application. Common solvents and carriers used in anti-fouling coatings are water, organic solvents (*e.g.*, acetone, xylene, toluene), alcohols (*e.g.*, ethanol, isopropanol), and glycol ether.[31] In a recent study, the use of dimethyl sulfoxide was recommended as a green solvent for anti-fouling applications.[32]

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These raw materials can be combined in various formulations and ratios to achieve specific performance requirements for different applications and environmental conditions. It is important to consider factors such as toxicity, environmental impact, regulatory compliance, and effectiveness when selecting raw materials for anti-fouling applications.

3. Classification of anti-fouling materials

Anti-fouling materials are classified based on their working mechanism, *e.g.*, anti-adhesion, cell adhesion prevention, cell detachment, or cytocidal and cytostatic action, as illustrated in Fig. 2.

Planktonic cells interact with surfaces by physical processes, including electrostatic interactions, which leads to bacterial adherence.[33] The mechanism by which hydrophilic polymer molecules chemically or physically adsorb to form anti-adhesion coatings prevents the reversible initial attachment by creating a steric and/or hydration barrier between the underlying substrate and the proteins and/or cells in solution above the surface. Coatings of various types are used to stop protein adsorption and fouling. Anti-adhesive biomaterials can be derived from natural sources such dextran, bovine serum albumin (BSA), chitosan, alginate, hyaluronic acid, and mannitol. Synthetically produced organic molecules such as PEG, PEO, and polyacrylamides are significant substitutes for natural polymers. The prevention of cell adhesion is crucial in various biomedical and industrial applications, particularly in the development of anti-fouling surfaces, medical implants, and drug delivery systems.

Several mechanisms are employed to effectively inhibit cell adhesion. Altering the surface chemistry or topography of materials can impede cell adhesion. For instance, hydrophilic surfaces repel protein adsorption and cell attachment due to reduced protein-surface interactions. Similarly, nanostructured or rough surfaces can create physical barriers that hinder cell adhesion. Zwitterionic polymers have a balanced surface charge because they have an equal amount of positively and negatively charged groups. Due to charge neutrality, this reduces electrostatic interactions and protein adsorption as well as cell attachment. It has been shown that zwitterionic compounds, including phosphorylcholine and sulfobetaine, are resistant to cell attachment and protein adsorption. A surface that interferes with cell adhesion hinders rather than eliminates the biological mechanism of cell attachment.

Strategies for preventing post-microbial attachment are also very important in combatting biofilms. Cells within the biofilm will gradually separate from it due to the breakdown of the biomolecules that maintain the microbial colony together, known as intercellular adhesion.[34] Cytostatic anti-fouling strategies aim to inhibit the proliferation or growth of fouling organisms without necessarily killing them. This approach is in contrast with cytotoxic methods, which involve the release of toxic substances to kill fouling organisms. Cytostatic anti-fouling is particularly relevant in environmentally sensitive areas, where the use of cytotoxic agents may have adverse effects on non-target organisms. Cytostatic anti-fouling strategies offer several advantages, including reduced environmental impact and the potential for long-term effectiveness.[35,36] However, challenges such as maintaining efficacy over extended periods, optimizing material compatibility, and ensuring cost-effectiveness remain areas of ongoing research and development. Integrating multiple cytostatic mechanisms and leveraging advances in materials science and surface engineering can lead to the development of highly effective anti-fouling solutions for various marine and biomedical applications.

Cytocidal anti-fouling strategies aim to kill or inhibit the growth of fouling organisms through the release of cytotoxic agents or through mechanisms that disrupt vital cellular processes. These approaches typically involve the use of chemicals or materials that are toxic to fouling organisms, effectively preventing their attachment and colonization. While cytotoxic anti-fouling strategies can be highly effective at preventing biofouling, they also raise concerns regarding environmental toxicity and the potential for unintended ecological consequences. Efforts are underway to develop safer and more sustainable alternatives, such as cytostatic or anti-adhesion anti-fouling strategies, which aim to inhibit fouling organism attachment without causing harm to the environment.

Balancing effectiveness with environmental considerations remains a key challenge in the development of cytotoxic anti-fouling technologies. Cell detachment anti-fouling strategies aim to facilitate the removal or release of fouling organisms from surfaces, thereby preventing their long-term adhesion and colonization. These strategies are particularly relevant in applications where periodic cleaning or maintenance is feasible or necessary, such as marine coatings, medical implants, and wastewater treatment systems.

The introduction of synthetic biomimetic polymethacrylates (SBPs) provides a low-cost, easily manipulated chemical

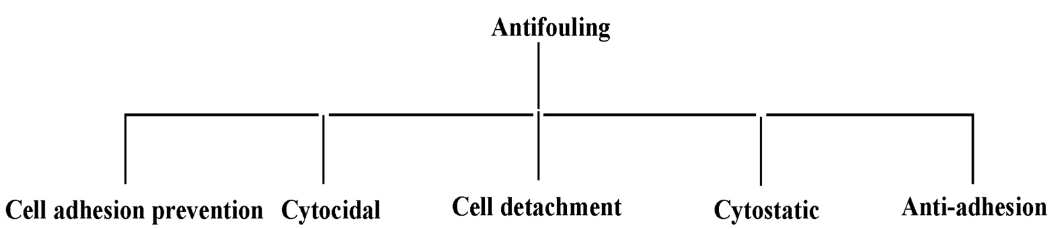

Fig. 2 Classification of anti-fouling materials.

platform for the development of a novel class of agents for the management and amplification of photosynthetic microorganisms. In heterotrophic bacteria, SBPs are cationic and membranolytic; they may also interact with the negatively charged cell walls and membranes of cyanobacteria or algae. SBPs prevent the growth of aquatic photosynthetic organisms that are of concern, such as green algae (*Chlamydomonas quadricauda*) and cyanobacteria (*Microcystis aeruginosa* and *Synechococcus elongatus*).[37]

Anti-adhesion anti-fouling strategies aim to prevent fouling organisms from adhering to surfaces in the first place, thereby inhibiting their attachment and colonization. These strategies focus on creating surfaces that repel fouling organisms or make it difficult for them to establish a foothold. Polymers must have a variety of physical and chemical characteristics to be selected as contenders for a given application. A few crucial characteristics of polymers that affect how they interact with biological environments are charge, isoelectric pH, glass transition temperature, biodegradability, structural and chemical stability, and biocompatibility. While the majority of manmade polymers are frequently non-biodegradable, all of the naturally occurring polymers listed above are biodegradable. Biodegradability can be engineered into synthetic polymers. Some notable instances are the invention of biodegradable polyurethane, copolymers of polylactic acid and polyglycolic acid, and the fact that PMMA is non-biodegradable but PHEA is biodegradable.[38,39] It should also be noted that biodegradability could compromise the stability of anti-fouling coatings, thereby rendering the surface incapable of resisting fouling. All of the above-mentioned polymers have the disadvantage in that they are not completely successful at preventing bio-fouling. In another study, surfaces brush-coated with PNIPAM were protein-resistant below its lower critical solution temperature (LCST) of 32 °C and non-resistive above the LCST, and therefore, it was unusable at *in vivo* temperatures.[40]

4. Anti-fouling methods

Anti-fouling methods can generally be divided into three categories: chemical, physical, and biological methods.

4.1 Chemical methods

Chemical anti-fouling (AF) methods generally employ AF paints with biocides, including silver, thiocyanate, copper powder,[41–43] Irgarol 1051,[44] zinc pyrithione,[45] and tributyltin (TBT). Some chemical methods are dependent on the use of metal ions in compounds that will become anti-fouling materials and prevent corrosion, and subsequently enhance the anti-adhesion ability of the surface. A dosage of ferrous chloride is used to coat a surface with a protective ferrous layer to prevent corrosion and reduce the adhesion and growth of marine fouling. Other studies suggested the use of composite and nano-composite materials such as graphene- or carbon nanotube (CNT)-modified TiO_2 composites as anti-fouling materials.[46,47]

4.2 Physical and mechanical methods

This method involves mechanical solutions for non-biocidal anti-fouling, such as brush systems or air bubbles, to prevent fouling. These systems disrupt the attachment process and help keep surfaces clean. Physical force or surface alterations, such as low drag, low adhesion, wettability, and microtextured structures, are used in physical-mechanical anti-fouling control methods to reduce microbe adhesion or accumulation on contact surfaces and prevent the formation of bio-fouling. Utilizing anti-biological or biomimetic surfaces derived from nature, such as lotus leaves, or shark, whale, and dolphin skin, holds promise for successfully controlling bio-fouling and providing opportunities for the development of non-polluting technologies. In addition, backwashing and pulsatile flow are one of the oldest anti-fouling physical techniques normally used for filtration membranes.[48]

4.3 Electrolytic system methods (cathodic protection)

This is one of the most commonly used systems to fight bio-fouling on ships. Electrolytic anti-fouling systems are a type of non-biocidal anti-fouling technology used to prevent the growth of marine organisms on submerged surfaces, such as boat hulls or underwater structures. These systems utilize the principle of electrolysis to release ions into the water, which creates an environment that is inhospitable to fouling organisms. The electrolytic setup is comprised of pairs of anodes, primarily made of copper and aluminum (or iron). The anodes are installed either in the sea chest or the strainer. DC electricity flows through the copper anodes, generating ions that travel with the seawater throughout the entire pipe system. The presence of copper ions in the seawater hinders the ability of marine organisms to adhere and reproduce on the pipes' surface. The purpose of the second anode is to stop the metal surface from corroding. The iron anodes prevent metal oxide films from corroding due to seawater's corrosive agents (sulphur).

This system additionally provides security for valves, condensers, engine cooling systems, and auxiliary equipment. A control panel assesses and supervises the performance of every anode in the system.[49–51] A comparative study examined the electrochemical behavior of a four-type titanium-supported anodic coating in the electrolytic anti-fouling of brine. They found that the electrochemical performance of the Ti–Ir–Ru anode was the most optimal, and the anode electrode material was ideal for anti-fouling by electrolyzing brine.[52] Fig. 3 illustrates the electrolytic anti-fouling system.

4.4 Ultrasonic method

This method is considered as a non-biocidal anti-foulant system. High-frequency waves are also used as a method to prevent marine growth in piping systems. These systems use ultrasonic waves to deter the attachment of fouling organisms. The ultrasonic waves create vibrations that deter organisms from settling on and attaching to ship hulls. Ultrasonic systems are known as one of the most highly effective methods to

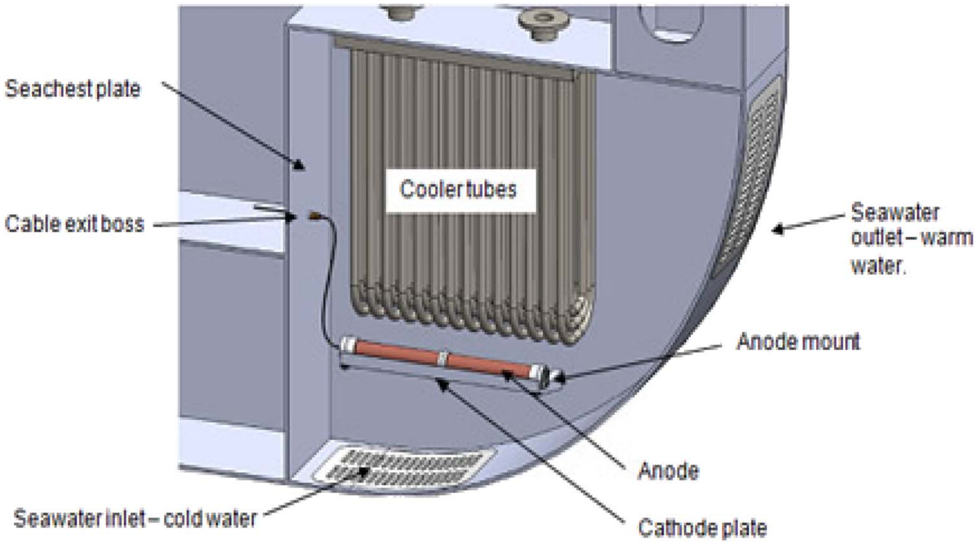

Fig. 3 Electrolytic anti-fouling system.

prevent bio-fouling. This method is said to reduce bio-fouling up to 80% using high frequency waves that alter the environment so it is unsuitable for organisms to settle, and by physically disrupting their adhesive deposits.

The ultrasonic technique involves the generation and transmission of high-frequency electrical impulses by a wave generator. The waves are transmitted through a coaxial cable to transducers that are located outside of the sea chests or strainers. The transducers contain piezoelectric ceramic crystals that produce an ultrasonic beam when activated by electrical impulses. The primary benefit of this system is that it does not require invasive measures, and no components come into contact with seawater. Furthermore, there are no harmful substances generated.[53,54] Fig. 4 illustrates a recommended ultrasonic anti-fouling system.[55]

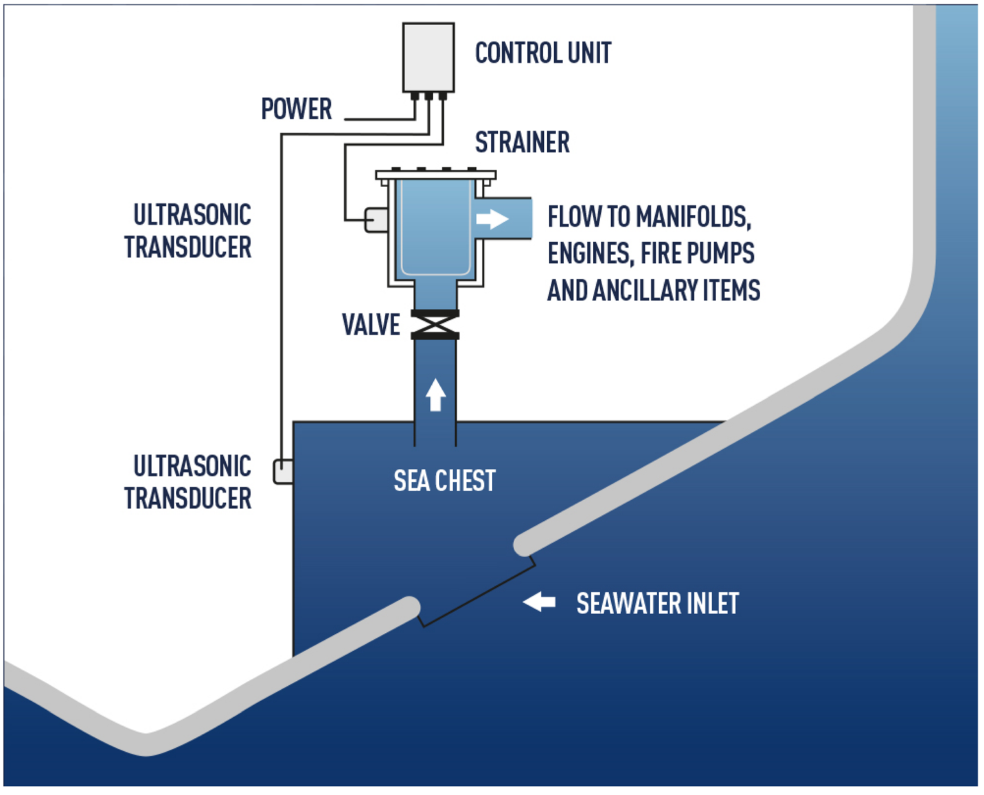

Fig. 4 Recommended ultrasonic anti-fouling system.[55]

4.5 Electro-chlorination method

Electro-chlorination is a method used to disinfect or control bio-fouling in water systems, including marine environments, by generating chlorine through electrolysis. Chlorine is a powerful oxidizing agent that effectively kills bacteria, algae, and other microorganisms, and also prevents the growth of marine-fouling organisms such as barnacles and mussels. The electro-chlorination system consists of an electrolysis cell or chamber where the electrolysis process occurs. This cell contains electrodes that are typically made of titanium coated with a mixed metal oxide (MMO) catalyst. A solution of seawater or brine is fed into the electrolysis cell as the electrolyte. The salt (sodium chloride) in the water serves as the source of chlorine ions for the electrochemical reaction. An electrical power source, such as a direct current (DC) power supply, is connected to the electrodes in the electrolysis cell.[56] When the power supply is activated, an electrical current will pass through the electrodes and the electrolyte solution. At the anode (positive electrode), chloride ions (Cl^-) in the electrolyte are oxidized to form chlorine gas (Cl_2) according to the following reaction:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

At the cathode (negative electrode), water molecules (H_2O) are reduced to form hydrogen gas (H_2) and hydroxide ions (OH^-):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

The chlorine gas produced at the anode dissolves in the surrounding water to form hypochlorous acid (HOCl) and hypochlorite ions (OCl^-), which are powerful disinfectants:

$$Cl_2 + H_2O \leftrightarrow HOCl + H + Cl^-$$

$$HOCl \leftrightarrow H + OCl^-$$

The chlorine generated through electrolysis acts as a disinfectant, killing bacteria, viruses, and other microorganisms present in the water. Additionally, it prevents the settlement and growth of fouling organisms on submerged surfaces by disrupting their cellular processes.[57] Titanium is used as the cathode material, whereas titanium coated with 100 micro-inches of platinum is used as anodes. Chlorine is generated at the anodes along with other elements to form sodium hypochlorite. A large amount of hydrogen gas is also produced, which should be safely evacuated. The total output of chlorine is a function of current rather than flow through the unit. Thus, adequate flow is required to ensure cooling and to prevent calcareous deposits.

Electro-chlorination systems are commonly used in various applications, including seawater desalination plants, ballast water treatment systems for ships, and cooling water systems for power plants. They offer several advantages, including effective disinfection, low chemical usage, and minimal environmental impact compared to traditional chemical disinfection methods.[58] However, careful monitoring and control of chlorine levels are necessary to ensure proper disinfection while minimizing the risk of chlorination byproducts and environmental harm.

5. Polymers for anti-fouling applications

Polymers and polymer composites are the basis for anti-fouling materials when physical methods are used. Polymer-based anti-fouling coatings are a type of non-biocidal anti-fouling solution that utilizes the physical and chemical properties of polymers to prevent the attachment of fouling organisms to submerged surfaces. These coatings create surfaces that are inhospitable to fouling organisms, reducing or eliminating the need for toxic biocides. The use of harmful biocides as anti-fouling materials led to thorough research to find eco-friendly alternatives. In research by Chiang and his coworker, an anti-fouling coating was developed by adding a non-toxic anti-foulant (butenolide) to a bio-based and biodegradable poly(lactic acid)-based polyurethane. The polymer degraded in seawater at a rate of 0.013 mg per cm^2 per day, and butenolide was released over a period of at least three months, demonstrating the polymer's suitability for eco-friendly anti-fouling applications.[59]

Numerous polymers have been explored and utilized in the development of anti-fouling coatings and materials due to their versatile properties and compatibility with various surface modification techniques. They are polyethylene glycol (PEG), poly(ethylene oxide) (PEO),[6] polyvinylpyrrolidone (PVP), polyzwitterione, polyethyleneimine (PEI), poly(methacrylic acid) (PMAA), polyurethanes, (PU), poly(dimethylsiloxane) (PDMS),[60] poly(methyl methacrylate) (PMMA), fluoropolymers (such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF), acrylic polymers, and chitosan. These polymers can be used alone or in combination with other materials and additives to develop multifunctional anti-fouling coatings and surfaces tailored to specific applications and environmental conditions.

Silicone-based coatings are widely used in fouling-release anti-fouling systems. These coatings create a low-surface-energy surface that is smooth, and to which fouling organisms cannot easily attach. Additionally, the water-repellent properties of silicone polymers are excellent, and these prevent the adhesion of marine organisms. However, the adhesion of silicon-based anti-fouling agents to the substrate is poor, and their static anti-fouling capabilities are deficient, which deteriorate their anti-fouling properties over time. Thus, a formulation of poly(dimethylsiloxane)-based anti-fouling added to epoxy resin (EP) and capsaicin (CAP) was used to enhance the interfacial adhesion and anti-fouling performance.[61] A smart self-healing silicone-based coating with dual anti-fouling and anti-corrosion properties was developed using a disulfide exchange reaction between the functionalized monomer lipoic acid-benzothiazole (LA-BTZ) and LA-modified polydimethylsiloxane (PDMS)-based polyurea-urethane. The multiple dynamic bonds in the backbone, flexible disulfide bonds, and strong cross-linked hydrogen bonds led to enhanced toughness (ultimate strength), stretchability, and self-healing properties.[62]

The development of optimal mechanical properties and anti-fouling characteristics in silicone-based coatings remains a difficult task, and therefore, a hybrid anti-fouling coating based on silicone and zirconia (ZrO_2) was developed. The results indicated that the characteristics of the coating are remarkable, and include high hardness, flexibility, wear resistance, and strong adhesion to the substrate in addition to outstanding self-cleaning capabilities, as well as its remarkable ability to resist fouling such as bacterial adhesion, protein attachment, diatom deposition, and biofilm formation.[63]

Another hybrid anti-fouling coating consisting of silicone elastomer and nanocomposite hydrogel was successfully prepared using silver nanoparticles (AgNPs). The applications for this hybrid coating in marine anti-fouling are promising.[64,65] A polydimethylsiloxane-polymethylmethacrylate (PDMS-PMMA) blend was used with silver nanospheres and titanium dioxide nanorods grafted onto a graphene oxide surface to produce marine anti-fouling coatings by a catalytic hydrosilation method. This coating is considered to be a non-toxic and non-stick nanocoating with various qualities such as superhydrophobicity, mechanical robustness, and fouling retardancy. This nanocoating offers high mechanical durability, low biodegradability, and optical density against different bacterial strains. Additionally, it exhibited non-toxicity against *Trichogaster lalius* fish and the bivalve *Brachidontes variabilis* model species. Higher nanofiller concentrations up to 5 wt% led to reduced water and fouling repellency due to particle clustering. The illustration below shows the preparation of a PDMS-PMMA/Ag-TiO_2-GrO hybrid nanocomposite *via* the solution casting method as a superhydrophobic and foul-release (FR) coating (Fig. 5).[66]

Silicone with zwitterionic polymers and carbamates can be used to create a low surface energy less than 30 mJ m^{-2}, and good fouling release properties in the range of 0.3–0.5 MPa. Zwitterions provided the coating with excellent fouling-resistance properties, and the anti-bacterial efficiency against Pseudomonas sp. was 94.86% so that the coating could inhibit the formation of biofilm and effectively prevent the adhesion of diatoms.[67] Silicone coatings can adhere to a variety of substrates commonly used in marine applications, including metals, fiberglass, plastics, and composites. They can be applied to hulls, propellers, sea chests, and other underwater surfaces to provide comprehensive anti-fouling protection.

Silicone-based coatings are known for their durability and resistance to environmental factors such as sunlight (UV radiation), saltwater, and harsh weather conditions. Because of these properties, they are suitable for long-term use in marine environments without significant degradation or loss of performance. Silicone-based anti-fouling coatings are typically non-toxic and environmentally friendly compared to traditional biocidal coatings, which may contain harmful chemicals. They do not release toxic substances into the water, and thereby reduce the risk of environmental pollution and harm to marine

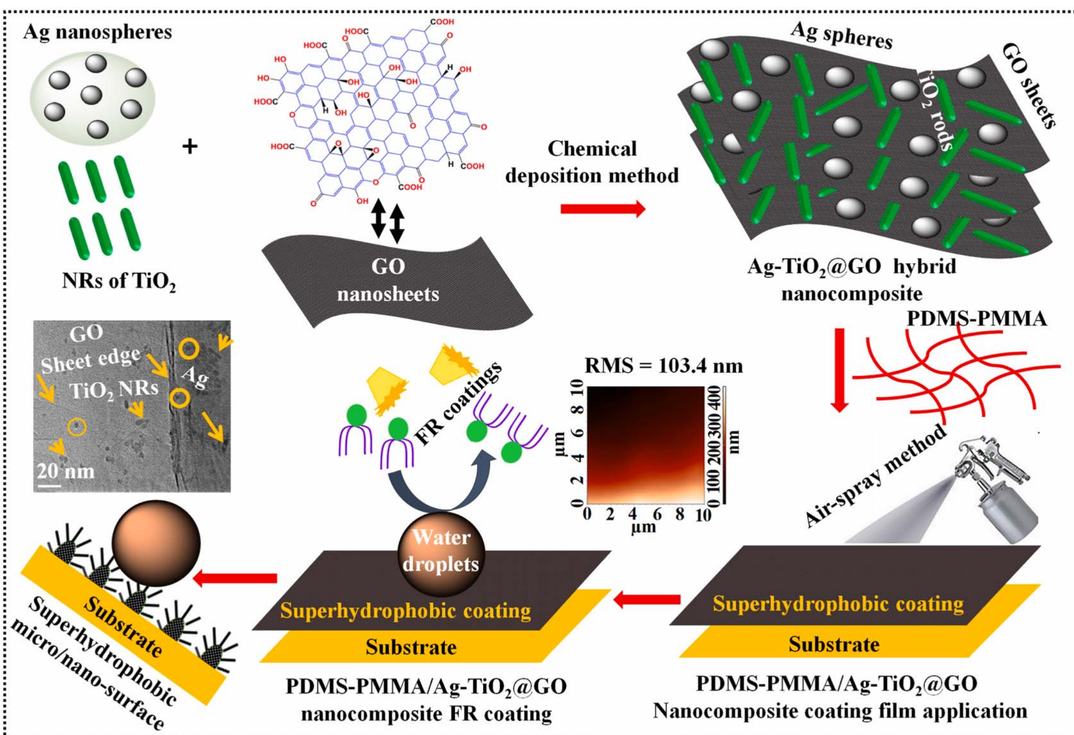

Fig. 5 Preparation stages of a PDMS-PMMA/Ag-TiO_2-GrO hybrid nanocomposite *via* the solution-casting method as a superhydrophobic and FR coating.[66]

ecosystems. Silicone coatings are relatively easy to apply using standard techniques such as spraying, brushing, or rolling. They require minimal surface preparation, and can be easily cleaned and maintained to restore their anti-fouling properties.[61,65,68–70]

A study by Lagerström *et al.* compared silicone foul-release coatings to traditional copper-based coatings in the Baltic Sea and found that copper emissions were reduced by over 90% when polymer-based alternatives were used. Even though most silicone foul-release coatings (FRCs) on the market are biocide-free, they may not be completely environmentally benign, simply for the lack of biocides. Nonetheless, FRCs are substantially less toxic compared to biocidal anti-fouling coatings, and their use should be promoted.[21]

Polysiloxane copolymer-based anti-fouling coatings utilize the properties of polysiloxane copolymers to prevent the attachment of fouling organisms to submerged surfaces. Polysiloxane copolymers, also known as silicone copolymers, combine the characteristics of silicone polymers with other monomers to create coatings with enhanced durability, flexibility, and fouling-release properties. Polysiloxane copolymers combine the properties of silicone and other polymers to create coatings with enhanced durability, flexibility, and fouling-release properties. These coatings can be tailored to specific applications and environmental conditions. Polysiloxane copolymer coatings exhibit fouling-release properties, creating surfaces that are resistant to fouling by marine organisms. Because of the smooth and low-energy-surface, fouling organisms cannot easily attach, and are easily dislodged by water flow or vessel movement. Polysiloxane copolymer coatings are inherently hydrophobic, repelling water and preventing the adhesion of fouling organisms. This property assists in maintaining a clean surface by minimizing the accumulation of water and debris.

Polysiloxane copolymers are chemically inert materials that are resistant to degradation by chemicals, acids, bases, and solvents. Thus, they are suitable for use in harsh marine environments where exposure to corrosive substances is common. Polysiloxane copolymer coatings are known for their durability and resistance to environmental factors such as sunlight (UV radiation), saltwater, and abrasion. This ensures long-term protection against fouling without significant degradation or loss of performance. Polysiloxane copolymer coatings exhibit flexibility and elasticity, allowing them to accommodate substrate movement and expansion without cracking or delamination. Thus, they are suitable for use on various substrates and in dynamic marine environments.

Polysiloxane copolymer coatings can adhere to a variety of substrates commonly used in marine applications, including metals, fiberglass, plastics, and composites. They can be applied to hulls, propellers, sea chests, and other underwater surfaces to provide comprehensive anti-fouling protection. Polysiloxane copolymer-based anti-fouling coatings are typically non-toxic and environmentally friendly compared to traditional biocidal coatings, which may contain harmful chemicals. They do not release toxic substances into the water, reducing the risk of environmental pollution and harm to marine ecosystems.[71–73]

Acrylic polymers are commonly used in anti-fouling coatings due to their versatility, durability, and adhesion properties. These polymers can be formulated to provide effective fouling resistance while maintaining environmental friendliness. The adhesion of acrylic polymers to a wide range of substrates commonly used in marine environments is excellent, and includes metals, fiberglass, concrete, and wood. This ensures that the coating firmly adheres to the substrate and can provide long-lasting protection against fouling.

Acrylic polymers are known for their durability and resistance to environmental factors such as sunlight (UV radiation), saltwater, abrasion, and weathering. Thus, acrylic-based anti-fouling coatings are suitable for use in harsh marine environments where exposure to corrosive substances is common. The flexibility and elasticity exhibited by acrylic polymers allows them to accommodate substrate movement and expansion without cracking or delamination. This ensures that the coating maintains its integrity and performance over time, even in dynamic marine environments.

Acrylic-based anti-fouling coatings are relatively easy to apply using standard techniques such as spraying, brushing, or rolling. They can be applied to new and existing surfaces with minimal surface preparation, reducing application time and costs. Acrylic polymers can be formulated with additives and modifiers to tailor their properties to specific anti-fouling requirements. For example, biocides, hydrophobic agents, fouling-release additives, and other ingredients can be incorporated into acrylic-based coatings to enhance their fouling resistance and performance. Acrylic-based anti-fouling coatings can be formulated to be environmentally friendly and non-toxic, minimizing the release of harmful chemicals into the marine environment. In particular, the volatile organic compound (VOC) emissions and environmental impact are lower for water-based acrylic formulations compared to solvent-based coatings.

Acrylic polymers can be used as standalone coatings or as part of multi-layer coating systems. They are compatible with other types of coatings, such as epoxy primers or barrier coatings, allowing for the creation of comprehensive anti-fouling solutions tailored to specific applications and substrates. Acrylic polymers offer a versatile and effective solution for anti-fouling coatings in marine environments. Their adhesion, durability, flexibility, ease of application, customization options, environmental friendliness, and compatibility with other coatings make them a popular choice for various marine applications, including ship hulls, offshore structures, and marine equipment.[8,10,74–76]

Sulfated bioactive polyphenols are new anti-fouling agents with low or non-toxic effects on the environment that can be a valuable alternative to toxic anti-fouling agents. Phenolic polymers are ideal candidates for marine coatings due to their chemical stability, lower volatility, and lower tendency for release from a polymer into the contact medium. Treatment of a surface with sulfated polymers might prevent mussels from attaching to surfaces.[77] An anti-fouling coating with self-healing and self-repairing capabilities is a very practical idea, but these types of coatings are normally associated with microcapsule aggregation problems due to their high surface energy. Thus, self-healing polyurethane-based coatings were developed to be used for anticorrosion and anti-fouling, with promising results in prolonging the service life of metals.[78]

Polyethylene glycol (PEG)-based anti-fouling coatings utilize the unique properties of PEG polymers to prevent the attachment of fouling organisms to submerged surfaces. PEG is a water-soluble polymer that forms a hydrated surface layer, which results in a reduction in the adsorption of proteins and other biomolecules that facilitate fouling. PEG-based coatings are known for their ability to resist protein adsorption and cell attachment, thus preventing fouling by microorganisms and accumulation of proteinaceous material on surfaces. This reduces the initial attachment of fouling organisms and assists in maintaining a clean surface over time. PEG polymers create a hydrated layer on surfaces, which reduces the adhesion of proteins and other biomolecules.[79] PEG polymers have a high affinity for water and readily absorb moisture from the surrounding environment, forming a hydrated layer on surfaces that acts as a barrier to fouling organisms.

As PEG is non-toxic and biocompatible, it is safe for use in marine environments without harming aquatic organisms. PEG-based coatings do not release toxic chemicals into the water, and therefore, the risk of environmental pollution and harm to marine ecosystems is reduced. PEG-based coatings can be applied to a variety of substrates using standard techniques such as spraying, brushing, or dipping. They adhere well to different surfaces, and can be easily integrated into existing anti-fouling systems or coatings.[80] PEG-based coatings can be combined with other additives or compounds to enhance their anti-fouling properties. For example, antimicrobial agents, bioactive compounds, or surface modifiers can be incorporated into PEG coatings to further deter fouling organisms.

PEG coatings exhibit long-term stability and durability in marine environments, resisting degradation from exposure to sunlight, saltwater, and harsh weather conditions. This ensures continued protection against fouling over extended periods without the need for frequent recoating or maintenance. The properties of PEG-based coatings, such as molecular weight, chain length, and surface density, can be tailored to specific applications and environmental conditions. This allows for customization of the coating to optimize its anti-fouling performance for different marine environments and substrates.[14–16,80,81]

Fluoropolymer-based anti-fouling coatings utilize the unique properties of fluoropolymers to prevent the attachment of fouling organisms to submerged surfaces. Fluoropolymers are resistant to fouling by marine organisms because they are highly hydrophobic and chemically inert materials. Fluoropolymers, such as polytetrafluoroethylene (PTFE) and perfluoroalkoxy (PFA), are highly hydrophobic and chemically inert materials. After an object is coated with these substances, surfaces are created with low surface energy and excellent water repellency that are resistant to fouling by marine organisms. Fluoropolymers have a low surface energy, which makes them highly hydrophobic and resistant to wetting by water. This property prevents the adhesion of water and fouling organisms on surfaces, reducing the likelihood of bio-fouling. Because fluoropolymers are chemically inert materials that are resistant to degradation by chemicals, acids, bases, and solvents, they are suitable for use in harsh marine environments where exposure to corrosive substances is common. Fluoropolymer coatings exhibit excellent water repellency, causing water to bead up and roll off surfaces. This self-cleaning effect assists in removing loosely attached organisms and debris so that surfaces remain clean and free from fouling.

Fluoropolymer coatings have a smooth surface with low friction that reduces drag and improves hydrodynamic performance. This can lead to fuel savings and increased efficiency for marine vessels. Fluoropolymer-based anti-fouling coatings are known for their long-term durability and resistance to environmental factors such as sunlight (UV radiation), saltwater, and abrasion. This ensures continued protection against fouling over extended periods without the need for frequent recoating or maintenance. Fluoropolymer coatings can adhere to a variety of substrates commonly used in marine applications, including metals, fiberglass, plastics, and composites. They can be applied to hulls, propellers, sea chests, and other underwater surfaces to provide comprehensive anti-fouling protection. Fluoropolymer-based anti-fouling coatings are typically non-toxic and environmentally friendly compared to traditional biocidal coatings, which may contain harmful chemicals. They do not release toxic substances into the water, reducing the risk of environmental pollution and harm to marine ecosystems.[46,82,83]

Hydrogel anti-fouling coatings are a type of polymer-based solution used to prevent the attachment of fouling organisms to submerged surfaces. These coatings utilize hydrogel polymers, which are water-swollen networks of hydrophilic polymer chains, to create surfaces that are resistant to fouling. Hydrogel coatings are water-swollen polymer networks that can release water into the surrounding environment. These coatings can mimic the properties of natural surfaces, such as the slippery surface of certain marine organisms, to deter fouling attachment. Bioactive compounds or additives can be incorporated into hydrogel polymers to enhance their anti-fouling properties. Hydrogel polymers have a high affinity for water,[84,85] which causes them to swell and form a hydrated layer on surfaces[86] that deters fouling organisms, as they prefer to attach to dry surfaces. Hydrogel coatings can inhibit the adsorption of proteins and other biomolecules onto surfaces, which is often the first step in the fouling process.[87,88]

Hydrogel coatings can be engineered to incorporate bioactive compounds or additives that deter fouling organisms. These compounds may include natural antimicrobial agents, enzymes, or chemicals that interfere with the settlement and growth of fouling organisms. Hydrogel coatings can be applied to a variety of substrates commonly used in marine applications, including metals, plastics, and composites.[86] They can be applied as thin films or coatings using techniques such as spraying, dipping, or brushing. Hydrogel anti-fouling coatings are typically non-toxic and environmentally friendly compared to traditional biocidal coatings, which may contain harmful chemicals. They do not release toxic substances into the water, reducing the risk of environmental pollution and harm to marine ecosystems. Some hydrogel polymers are biocompatible, meaning they are compatible with living tissues and

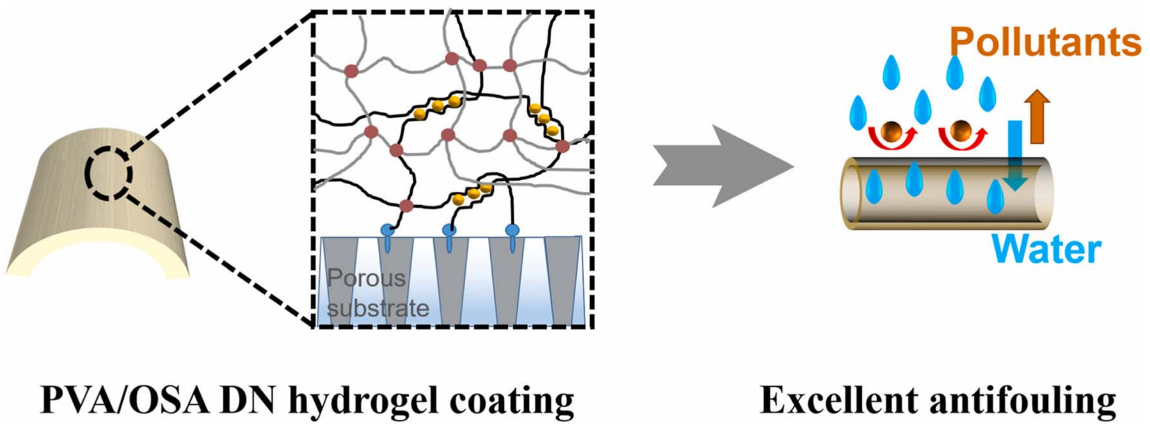

Fig. 6 Working mechanism of PVA/OSA double-network hydrogel.[92]

organisms. This property can be beneficial for applications where direct contact with marine organisms is unavoidable, such as in aquaculture or marine biology research.

The properties of hydrogel coatings, such as swelling behaviour, mechanical strength, and surface chemistry, can be tailored to specific applications and environmental conditions. This allows for customization of the coating to optimize its anti-fouling performance.[86,89–91] Hydrogel-based anti-fouling materials were created by crosslinking a copolymer composed of the capsaicin derivative *N*,*N*′-((4,5,6-trihydroxy-1,3-phenylene)-bis(methylene))diacrylamide (TPA), along with lipophilic and hydrophilic monomers. This hydrogel demonstrated anti-protein properties due to its hydrophilicity, while the capsaicin derivative provided the hydrogel coating with outstanding algae inhibition performance. The anti-fouling performance was significantly improved by this capsaicin derivative (TPA)-functionalized hydrogel coating.[87]

Traditional hydrogels often exhibit poor mechanical properties and lack long-term application value. Thus, some researchers prepared hydrogel for underwater anti-fouling applications based on PEG for excellent mechanical properties and satisfactory anti-fouling performance.[89] Anti-fouling double-network hydrogel coatings for polytetrafluoroethylene (PTFE) hollow fiber membranes were prepared through silane grafting using polyvinyl alcohol/oxidized sodium alginate (PVA/OSA). The exceptional anti-fouling performance of PVA/OSA is mainly attributed to the beneficial interfacial electrostatic interactions and the hydration layer formed on the membrane surfaces. PVA/OSA hydrogel coatings maintained high hydrophilicity, structural integrity, and operational stability even after prolonged exposure to strong acidic and alkaline solutions. The working mechanism of a PVA/OSA hydrogel is shown in Fig. 6.[92] Table 1 provides a comparative overview of the different polymer types in terms of efficacy, cost, and ecological safety.

Table 1 Comparison of polymer-based anti-fouling coatings

Polymer type	Anti-fouling mechanism	Efficacy	Cost	Ecological Safety	Durability	Key limitations
Silicone-based (PDMS, polysiloxane copolymers)	Fouling-release	High	Moderate to high	Low toxicity, environmentally friendly	Moderate to high	Poor adhesion to substrate, needs surface priming
Fluoropolymers (PTFE, PVDF, perfluoropolyethers)	Hydrophobic fouling resistance	Very high	High	Non-toxic, stable, but long-term persistence raises concerns	High	Expensive, potential bioaccumulation risk
Polyethylene glycol (PEG) coatings	Hydration barrier prevents protein adsorption	Moderate	Low	Biodegradable, non-toxic	Moderate	Less effective under harsh marine conditions
Acrylic-based coatings	Hydrophobic and fouling-release	Moderate	Low to moderate	Low toxicity, customizable	Moderate	Can degrade under UV exposure
Hydrogel-based polymers (cross-linked PEG, zwitterionic coatings)	Bio-inspired hydration layer	High	Moderate	Biocompatible, eco-friendly	Moderate	Mechanical fragility under marine conditions
Polyurethanes (PU-based coatings)	Hybrid anti-fouling mechanisms	High	Moderate	Low toxicity, highly tunable	High	Can degrade under harsh environmental conditions

6. Testing of polymer-based anti-fouling materials

Testing polymer-based anti-fouling materials involves evaluating their effectiveness in preventing the attachment of fouling organisms to submerged surfaces. Various methods and techniques are employed to assess the fouling resistance and performance of these materials. The International Organization for Standardization (ISO) has developed standards (*e.g.*, ISO 15181) outlining procedures for evaluating the anti-fouling performance of marine coatings. These standards provide guidelines for sample preparation, testing conditions, and performance assessment. The American Society for Testing and Materials (ASTM) has also established standards (*e.g.*, ASTM D5618) for anti-fouling testing methods, including laboratory and field procedures.

Conducting comprehensive anti-fouling testing using a combination of laboratory, field, and standardized methods, researchers and manufacturers can assess the performance and durability of anti-fouling coatings, and develop effective solutions for preventing bio-fouling in marine environments. Researchers and manufacturers can assess the fouling resistance and performance of polymer-based anti-fouling materials and optimize their formulations for specific marine applications by utilizing the following testing results.[93,94]

6.1 Water uptake

The water uptake of anti-fouling coatings refers to the amount of water absorbed by the coating when submerged in water. Understanding water uptake is important because it can affect the performance and durability of the anti-fouling coating, as well as its ability to resist fouling by marine organisms. Water uptake can lead to the formation of a hydrated layer on the surface of the coating. This hydrated layer can affect the interaction between the coating and fouling organisms, influencing their ability to attach and proliferate.

Some anti-fouling coatings, especially hydrogel-based coatings, may swell when exposed to water. This swelling behavior can alter the physical properties of the coating, such as its thickness, porosity, or mechanical strength, which may impact its fouling resistance. Water uptake can facilitate the release of bioactive compounds incorporated into the anti-fouling coating. These compounds may include biocides, fouling-release agents, or other additives designed to deter fouling organisms.

The rate and extent of compound release can affect the efficacy and longevity of the anti-fouling protection. Excessive water uptake can compromise the integrity and durability of the anti-fouling coating over time. Water-induced swelling and degradation may lead to delamination, blistering, or loss of adhesion, which will reduce the effectiveness of the coating in preventing fouling. Water uptake can also impact the environmental performance of anti-fouling coatings. Excessive leaching of bioactive compounds into the surrounding water can pose environmental risks and regulatory concerns, potentially leading to pollution or harm to aquatic ecosystems.

To evaluate the water uptake of anti-fouling coatings, researchers typically conduct water immersion tests or moisture absorption tests under controlled laboratory conditions. These tests involve submerging coated samples in water for a specified period, and then measuring the weight gain or dimensional changes resulting from water absorption. By quantifying water uptake and understanding its effects on coating performance, researchers can optimize the formulation and design of anti-fouling coatings for enhanced durability and fouling resistance in marine environments.[9,95]

6.2 Contact angle measurement

Contact angle measurement is a common technique used to assess the surface wettability and hydrophobicity/hydrophilicity of materials,[96–98] including anti-fouling coatings. The contact angle is the angle formed between a liquid droplet and the surface of a solid material. For anti-fouling coatings, a higher contact angle indicates greater hydrophobicity, meaning that water droplets will bead up and roll off the surface more easily, potentially deterring fouling organisms from attaching.

Contact angle measurements provide quantitative information regarding how well a liquid wets the surface of a coating. A low contact angle ($<90°$) indicates high surface energy and hydrophilicity, meaning that water spreads out and wets the surface readily. In contrast, a high contact angle ($>90°$) indicates low surface energy and hydrophobicity, causing water droplets to bead up and roll off the surface. Hydrophobic surfaces with high contact angles are generally more resistant to fouling by marine organisms.[99–102] When water is unable to effectively wet a surface, there is a greater degree of difficulty for fouling organisms, such as algae, barnacles, and mussels, to attach and colonize the surface.

Changes in the contact angle over time can indicate changes in the surface properties and durability of the anti-fouling coating. For example, a decrease in contact angle may suggest surface degradation or contamination, which could compromise the effectiveness of the coating in deterring fouling. Contact angle measurements can be used to compare the effectiveness of different anti-fouling coatings or formulations. Researchers can evaluate which coatings exhibit the highest levels of hydrophobicity and fouling resistance by measuring the contact angles of water droplets on various coated surfaces.

Contact angle measurements are usually conducted with specialized instruments called contact angle goniometers. These instruments dispense a small droplet of liquid, typically water, onto a coating's surface and measure the angle formed between the droplet and the surface using imaging techniques.[103–105] Contact angle measurements offer valuable insights into the surface properties of anti-fouling coatings, and provide aid to researchers in optimizing their formulations to improve fouling resistance in marine environments.[106]

6.3 Leaching of biocides

Leaching testing of biocides in anti-fouling coatings involves assessing the release of biocidal compounds from the coating into the surrounding water under simulated or real-world conditions. This testing is important for evaluating the environmental impact and efficacy of anti-fouling coatings, as well as ensuring regulatory compliance.[107–110] Here are some common approaches to leaching testing of biocides from anti-fouling coatings:

(i) Static immersion tests: coated substrates are submerged in containers of seawater or artificial seawater under controlled laboratory conditions for a specified period. The water is periodically sampled and analyzed for the presence and concentration of leached biocides using analytical techniques such as high-performance liquid chromatography (HPLC) or mass spectrometry.[111]

(ii) Dynamic flow-through test: water is continuously circulated over coated substrates in a flow-through system to mimic natural water movement and exchange. Leachate samples are collected at various time intervals and analyzed for biocide concentrations to assess leaching rates.

(iii) Microcosm experiments: coated substrates are placed in small-scale aquatic environments, such as tanks or mesocosms, containing natural or simulated seawater. The behavior of leached biocides and their impact on aquatic organisms and ecosystems are monitored over time.

(iv) Mesocosm studies: larger-scale experiments are conducted in semi-natural or controlled outdoor environments, such as enclosed ponds or coastal enclosures, to assess the fate and effects of leached biocides on marine ecosystems under more realistic conditions.

(v) Weathering chambers: coated substrates are exposed to simulated environmental conditions, including sunlight (UV radiation), temperature fluctuations, and immersion in seawater, to accelerate the degradation and leaching of biocides. The release of biocides is monitored over time to assess the durability and environmental stability of the coating.

(vi) Submerged exposure: coated panels or structures are deployed in marine environments, such as harbors, marinas, or coastal waters, for extended periods to assess biocide leaching under real-world conditions. Water samples are collected at regular intervals from the vicinity of the coated surfaces, and biocide concentrations are measured.[112]

(vii) Fate and transport models: computational models are used to simulate the release, dispersion, and fate of biocides in marine environments based on the physical and chemical properties of the coating, water flow dynamics, and environmental factors. These models can predict biocide concentrations and distribution patterns, which are factors that can be used to estimate environmental risk.[113–115]

Testing for biocides leached from anti-fouling coatings provides valuable data for assessing environmental impacts, optimizing coating formulations, and ensuring compliance with regulatory requirements. By assessing the release behavior of biocides under various conditions, researchers and manufacturers can create anti-fouling coatings that effectively prevent fouling and minimize environmental risks.[110,116]

6.4 Raft testing

Anti-fouling raft testing involves evaluating the performance of anti-fouling coatings or materials in real-world marine environments using specially designed raft structures. These tests are conducted to assess the ability of anti-fouling coatings to prevent fouling by marine organisms, such as algae, barnacles, and mussels, under natural conditions. Anti-fouling raft structures are typically constructed using buoyant materials such as foam, plastic, or wood that are assembled into a raft-like configuration. The raft may include multiple panels or sections coated with different anti-fouling formulations or materials for comparative testing.

Anti-fouling coatings or materials are applied to the surface of the raft panels according to the test protocol. The coatings may be applied using standard techniques such as spraying, brushing, or dipping to ensure uniform coverage of the substrate. The anti-fouling raft is deployed in a selected marine environment, such as a harbor, marina, or coastal area, where fouling pressure is expected to be high. The raft is anchored or tethered to prevent drifting and to ensure consistent exposure to fouling organisms. The raft remains submerged in the water for an extended period, typically several weeks to several months, to allow fouling organisms to colonize and grow on the coated surfaces. During this time, the raft is periodically monitored to assess fouling accumulation and coating performance. Fouling accumulation on the coated raft panels is periodically assessed through visual inspections or quantitative measurements. This may involve recording the abundance and diversity of fouling organisms, as well as the extent of coverage on the coated surfaces.

The data collected from the raft testing, including fouling observations, coating performance, and environmental conditions, are analyzed to evaluate the effectiveness of the anti-fouling coatings. Statistical analyses may be performed to compare different coatings or treatments and identify factors influencing fouling resistance. Based on the results of the raft testing, adjustments may be made to the anti-fouling formulations, application methods, or environmental conditions to optimize coating performance. This iterative process may involve conducting additional raft tests to validate improvements and refine the anti-fouling strategies. Anti-fouling raft testing provides valuable insights into the real-world performance of anti-fouling coatings and materials, and assists researchers and manufacturers in developing effective solutions for fouling prevention in marine environments. Simulating natural conditions and assessing fouling resistance in the field, raft testing complements laboratory-based assays and accelerates the development and validation of anti-fouling technologies.[117]

6.5 Polishing test

A polishing test for anti-fouling involves evaluating the ability of an anti-fouling coating to maintain its effectiveness over time, particularly in terms of preventing the attachment of marine organisms to the surface of a vessel's hull. Suitable test panels, typically made from materials commonly used in marine applications such as fiberglass or metal, are prepared. These panels are coated with the anti-fouling product being tested. The test panels are submerged in water under conditions that simulate real-world marine environments. Factors such as water temperature, salinity, and sunlight exposure may be controlled to mimic different geographic locations and seasons.

The panels are left submerged for a predetermined period, which can vary depending on the specific requirements of the test and the intended duration of protection for the anti-fouling coating. At regular intervals during the test period, the panels are removed from the water, and the extent of fouling is assessed. This assessment may involve visually inspecting the panels for the presence of organisms such as barnacles, algae, and mussels. Additionally, measurements of fouling density and biomass may be taken.

The effectiveness of the anti-fouling coating is determined based on the degree of fouling observed on the test panels compared to control panels that were not coated with the anti-fouling product. Factors such as the type and density of fouling organisms and the ease of removal of fouling may be considered in the evaluation. To ensure reliability and reproducibility of results, the polishing test may be repeated multiple times under consistent conditions, and statistical analysis may be performed to assess the significance of any differences observed.[118–122]

6.6 Atomic force microscopy

Atomic force microscopy (AFM) can be a valuable tool for studying anti-fouling properties at the nanoscale level. AFM can provide high-resolution images of the surface topography of materials, including anti-fouling coatings. By examining the surface roughness and morphology at the nanoscale, researchers can gain insights into how the surface features influence fouling resistance. AFM can be used to directly visualize and quantify fouling on surfaces. By scanning the surface with an AFM tip, researchers can measure the height and distribution of fouling organisms, such as bacteria, algae, or biofilms, attached to the surface. This allows for assessment of the effectiveness of anti-fouling coatings in preventing fouling attachment.

AFM can also determine the mechanical properties of surfaces, such as adhesion strength and stiffness. This information can be crucial for understanding the interactions between fouling organisms and anti-fouling coatings. For example, a more compliant surface may make it more difficult for fouling organisms to adhere. Dynamic studies can be performed with AFM to investigate the response of anti-fouling coatings to external stimuli, such as shear forces or changes in environmental conditions. This can assist researchers in understanding how anti-fouling properties evolve over time and under different circumstances.

Functionalized AFM probes can be used to study molecular interactions between anti-fouling coatings and fouling organisms or molecules. This can provide insights into the underlying mechanisms of anti-fouling action and assist in the design of more effective anti-fouling materials. AFM offers a powerful tool for studying anti-fouling properties at the nanoscale, providing valuable information for the development and optimization of anti-fouling coatings for various applications, including marine vessels, medical devices, and water treatment systems.[123]

6.7 Bacterial adhesion

Studying bacterial adhesion is crucial for assessing the effectiveness of anti-fouling coatings, especially since bacteria are often the initial colonizers of surfaces and can facilitate the attachment of other fouling organisms. Bacterial adhesion tests for anti-fouling coatings are crucial for evaluating the ability of these coatings to resist bacterial attachment, which is often the first step in bio-fouling formation. An overview follows of common methods used for bacterial adhesion testing in the context of anti-fouling.

The testing begins by applying the anti-fouling coatings onto substrates such as glass slides, metal coupons, or polymer surfaces, ensuring uniformity and appropriate curing. Control samples without anti-fouling coatings are also prepared for comparison. Then, a bacterial strain relevant to the intended application or environment is selected. These may include marine bacteria or species commonly found in aquatic environments. The bacteria are cultured to reach a desired cell density and physiological state.[123–125] Static bacterial adhesion can by investigated by two methods:

(i) Immersion test: coated samples are immersed in a bacterial suspension for a specified period, typically ranging from hours to days. After incubation, non-adherent bacteria are removed by rinsing or gentle agitation.

(ii) Incubation on agar plates: coated samples are placed onto agar plates inoculated with bacteria and incubated under controlled conditions. After incubation, the number of bacterial colonies adhering to the samples is quantified by colony counting.

Dynamic bacterial adhesion assays can be performed by two methods:

(i) Parallel plate flow chamber assay: this method simulates hydrodynamic conditions encountered in real-world environments. Bacterial suspensions are continuously flowed over coated samples, and the rate of bacterial adhesion is quantified by measuring the number of adherent cells over time.

(ii) Rotation disk or cone and plate assay: in these assays, a coated sample is attached to a rotating disk or cone and submerged in a bacterial suspension. The rotation generates shear forces, simulating fluid flow, and bacterial adhesion is assessed in a manner similar to that of the parallel plate flow chamber assay.

The quantification of bacterial adhesion can by investigated by direct counting, where the bacteria can be visualized and counted using microscopy techniques such as epifluorescence microscopy or scanning electron microscopy, or by biomolecular assays where techniques such as fluorescence labeling or qPCR can be used to quantify bacterial attachment by targeting specific bacterial biomarkers or genes. The analysis of a bacterial adhesion test is normally dependent on comparison between the extent of bacterial adhesion on coated surfaces to that on control surfaces. Factors such as the number of adherent bacteria, biofilm formation, and surface coverage are evaluated to assess the effectiveness of the anti-fouling coating. Conducting bacterial adhesion tests allows researchers to determine the efficacy of anti-fouling coatings in preventing bacterial attachment. This is essential for mitigating bio-fouling on various surfaces, including marine vessels, underwater structures, and medical implants.

7. Conclusion

Polymer-based anti-fouling coatings offer several advantages over traditional biocidal coatings, including environmental friendliness, long-term effectiveness, and compatibility with various substrates. However, they may require careful surface preparation and application to ensure optimal performance, and their effectiveness can vary depending on factors such as water conditions, substrate type, and fouling pressure. Ongoing research and development efforts continue to improve the performance and durability of polymer-based anti-fouling coatings for a wide range of marine applications.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts of interest to declare for this work.

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