



An overview of controlled-biocide-release coating based on polymer resin for marine antifouling applications

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Abstract

Biofouling is one of the major worldwide problems associated with the vessel due to its accumulation with the surface of the ship hull. The biofouling is the main origin of the coating's deterioration that ultimately leads to bio-corrosion, roughness and drag, resulting in an enormous increase in the fuel consumption. Although Tributyltin (TBT) has been used as a pioneer class of antifoulant to overcome this problem, however, after the legal restriction on TBT, some biocides have been used as its alternatives. These biocides are potentially harmful to the environment due to the higher release rate in the aquatic environment. This review paper focuses on the progress made in eco-friendly antifouling coating techniques, using control biocide release principal for marine application. The three main strategies, hydrophilic, hydrophobic, and biodegradable antifouling coating, are reviewed. Biodegradable antifouling coating is a new promising route based on the combination of eco-friendly biocide with dynamic surfaces by utilizing degradable polyurethane, polyester acrylate, and modified polyester based polymers. They are used as a carrier of antifoulant, which control the release rate and also show excellent antifouling activity in the marine coatings due to tunability, sustainability, and mechanical performance, therefore, they have a longer shelf period. Moreover, this review focuses on the challenges associated with vessel surface coating and their possible solutions.

Keywords Biofouling · Antifouling coating · Biocides · Hydrophilic · Hydrophobic · Biodegradable

Introduction

The word fouling has been coined on any substrate of undesirable formation (bacteria, algae, and mussel) [1]. The accumulation of marine organisms (both micro and macro-organisms) on ship hull surfaces have adverse surface effects such as liquid frictional resistance, corrosion rate, surface roughness, fuel consumption surge, and so on [2, 3]. Marine animals may also be transported by ship transport into non-native ecosystems. Marine biofouling is a global problem, costing billions of dollars annually in transport [4]. Antifouling (AF) coating is very crucial for marine biofouling

inhibition, due to the release of toxic material that impedes the growth of accumulated organisms, enables maintaining the surface [5–13]. Several toxic materials like arsenic, mercury and copper used in the paint for ship coating in the last decade. Similarly, tributyltin (TBT) was also incorporated into the self-polishing copolymer that exhibited an efficient performance against biofouling, that resulted in an increase of the dry-docking interval [14, 15]. The concentration of TBT in the seawater has been increased since 1970 due to the higher use of TBT-based antifouling coating, which induced adverse effects on the non-target species, as a result, it was banned worldwide in 2008. Despite the biocide based on metal or non-metal, antifouling agents have been used as an alternative to TBT based antifouling paint. Such biocides are very useful for marine biofouling but are potentially toxic to non-target species in seawater because of their higher release rate [16–19].

Because of this global problem, recent research focuses on environmentally friendly alternatives to ecological toxicological problems related to the use of toxic AF coatings, such as hydrophilic and hydrophobic antifouling coating [4].

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Hydrophilic antifouling coatings which prohibit or delay the adherence of marine biological species from adhering to ship hulls. Hydrophobic coatings, including fluoropolymers and silicone compounds, provide an environmentally friendly alternative that can be used for extended periods [20]. Fouling release (FR) coating technology functions by prohibiting fouling of settlements and producing ultra-smooth self-cleaning surfaces. Coating strategies with noble metal NPs and metal oxides may be efficient ways for preventing fouling due to their durability against microbial attacks [21–23]. Between these components, Cu_2O and ZnO are conveniently produced from low-cost, supposedly secure natural sources and therefore are appropriate for long term comprehensive studies [24]. Designated NPs will boost different properties in coating compositions, including antifouling (AF), mechanical and optical properties, permeability and wettability [25–27]. Therefore, scientists have recently followed the incorporation of nanocomposite biocide in hydrophilic and hydrophobic materials in micro and macrofouling in field test and assay, indicating that this is an excellent strategy for regulating the release rate and showing excellent antifouling activity [28–31].

Additionally, scientists have also introduced biocide into biodegradable polymers that are used as a carrier, resulting in relatively show release in marine water due to their hydrolyzable ester groups. As a result, it allowed the coating to slowly peel and showed improved antifouling behavior [32–39]. The Biodegradable polymer process occurs throughout the seawater immersion due to hydrolytic and enzymatic degradation. On the other hand, biodegradable polymers may undergo hydrolytic and enzymatic cleavage of the backbone, resulting in small molecules that ultimately develop into water and carbon dioxide after a certain period. The contaminated particles of the degradable polymer are much smaller; therefore they have no negative impact on the environment [40–42].

Legislation and laws are becoming complicated with the use of antifouling material that can impact on the marine environment. Under these difficulties, developing sustainable and wide-ranging advance antifouling materials is currently a global challenge. This review paper focuses on the recent development of strategies applicable to control the release of biocides and their antifouling activity. The aim of this study is to provide a critical understanding of an important area of sustainability-driven chemical research in which biocide has been used to improve green technology. We have discussed various approaches, including the incorporation of nanocomposite biocide in hydrophilic and hydrophobic antifouling coating, its release and antifouling activity. We have also highlighted the promising qualities of biodegradable polymers as an antifoulant carrier along with their release control, and antifouling activity.

Marine biofouling

Marine biofouling is composed of approximately four thousand different kinds of worldwide species [43]. The process of biofouling may be classified into two groups (1) micro-fouling and (2) macro-fouling. The microfouling is mainly caused by a microorganism such as bacteria and diatoms, while macro-fouling is caused by macroorganisms such as barnacles, algae, bryozoans, mussels, and seaweed, as shown in Fig. 1A [44]. It is well known that microorganisms accumulated on the biotic and abiotic surface, initially colonized on a surface and formed a biofilm [45]. The colonization of the biofilm formation process possesses in the initial and irreversible manner. The initial phase is a fundamentally direct attraction of microorganisms on the surface. The Initial attachment is controlled by a physical adhesion between the microorganism and the substrate [46, 47]. In the irreversible process, bacteria attach directly to the surface due to the low quantity of carbon level in the seawaters. Bacterial cells form biofilms on the surface and then disperse when they are mature or immature [48, 49]. Microorganisms colonies made up of larvae of certain species of barnacles, ascidian larvae, mollusks, and polychaete form biofilm components and possess a very strong settlement on the surface [50]. While microorganism secretes Extracellular Polymeric Substance (EPS), which consist of protein and polysaccharide, Moreover, the concentration of dissolved oxygen in seawater also increased the concentration of EPS, thus increasing the adhesion of biofilm adhesion by polysaccharide and dissolved oxygen [51].

Effect of biofouling

The marine organisms accumulated on the surface of a ship hull, have a bad economic and environmental effect on maritime industries, as shown in Fig. 1B [52]. Therefore, the shipping industry consumes billions of dollars every year due to biofouling [53]. When an organism attaches to the vessel hull, so the surface becomes smoothen, which increased drag; consequently, the speed of the ship is reduced, and the hydrodynamic weight increases. Therefore the world fleet fuel consumption is increased by biofouling organisms [54]. As a result, the huge amount, i.e., 1050 million tons of carbon dioxide, 25 million tons of nitric oxide, and 15 million tons of sulfur oxides emissions are recorded annually. Furthermore, it causes soil damage and acidic rain, atmospheric pollution, and shows serious environmental problems [55–57]. The increased consumption of fuel the expenses of cruise ships increased up to 77% due to the biofouling, not only in price increased but also shortened the dry docking time. The treatment of wastewater which is contaminated by the release of antifouling (AF) additives in water, that costs approximately €

3.5 billion which is consumed by international maritime transport for this purpose. The global shipping crises increased in 2012 and 2013 because of German national merchant reduced to 200 ships due to increasing fuel expenses [57], and due to the elastomeric coating applied on the largest vessel, which cost was very high for dry-docking [58]. Moreover, the non-indigenous species accumulate on the various hull locations and reach on the dry docking and ballast water. Hence, they attack the native organism and spread various diseases [59].

Development of antifouling technology

In 1908, for first-time spirit based varnish paint was applied at the bottom of the vessels. Meanwhile, mercury oxide based paint developed in different polymers, where mercury oxide

dispersed in turpentine and alcohol, which was found to be durable for 9 months [58].

In the twentieth century, the US Navy introduced rosin, which had additive properties and used as shellac. Therefore copper or mercury-based blended with rosin increased the antifouling activity, but they were toxic [61].

In the middle of the twentieth century, the organotin composite TBT showed an excellent antifouling property, which was reported by Van Der Kerk’s team. TBT biocidal composite eroded and hydrolysis by releasing toxic material in the marine environment. Initially, TBT based compound used with advanced copper antifouling composite coating and then pure TBT based compound utilized in the whole AF system [62]. TBT self- polishing coatings (TBT–SPC) was developed in 1958, which composed TBT acrylate ester used as an antifouling coating. In 1964 TBT methyl methacrylate and TBT acrylate were patented by James [63].

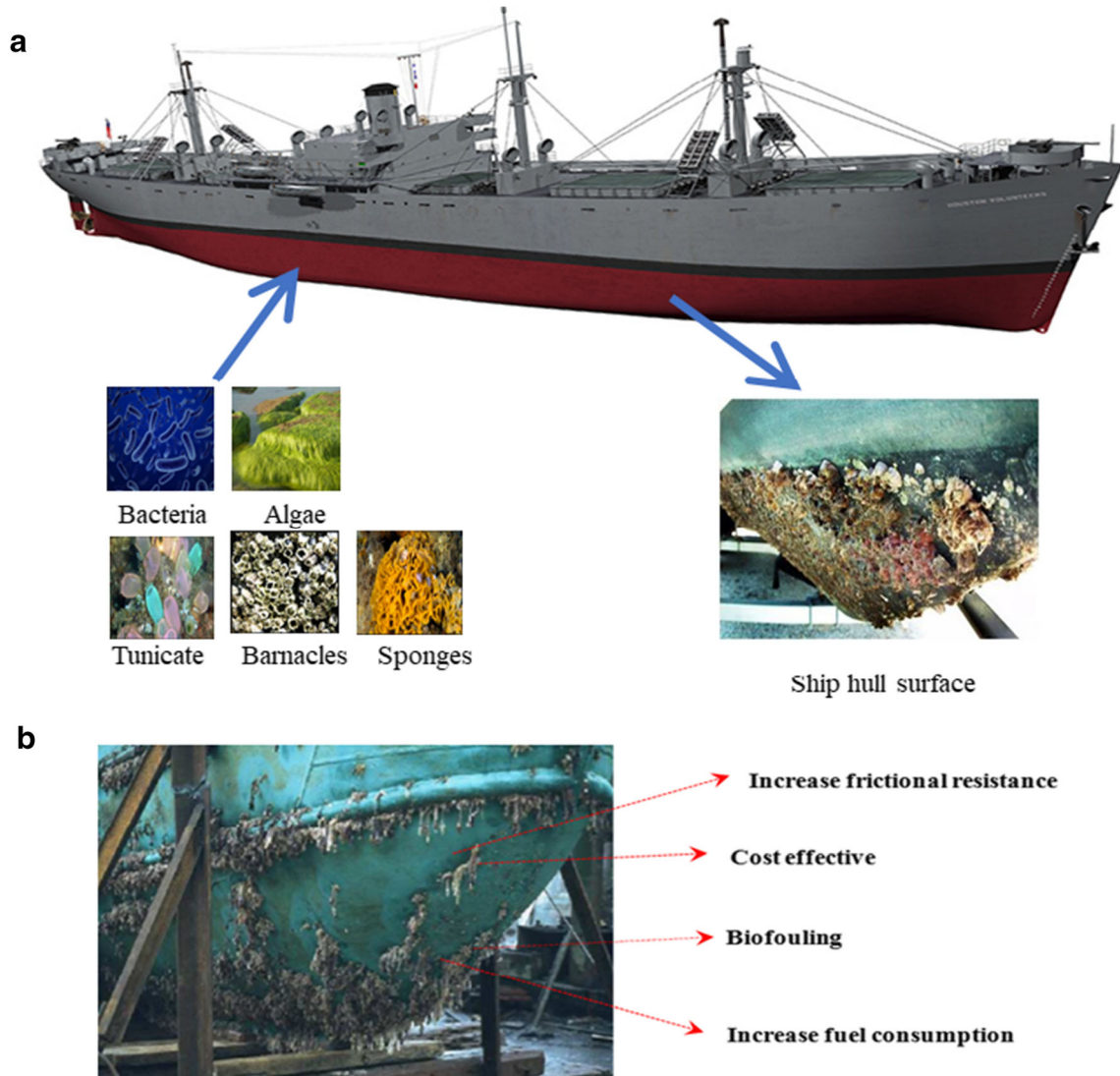


Fig. 1 a Schematic illustration of the marine micro and macro-fouling steps in the natural seawater [60]. b The biofouling accumulated on the surface of the ship [61]

TBT SPC based antifouling has different benefits such as decreased fuel consumption, broad release over time, and keeps hydrodynamic profile smooth during sailing [64, 65]. In 1990 TBT SPC was successfully painted more than 70% world fleet ship hull. However, TBT SPC was affected by non-targeted organisms because they disrupt enzymatic function and essential metabolite; as a result, organisms died [66]. Antifouling based on TBT SPC has various advantages such as lower fuel consumption, large release over time, and keeps the hydrodynamic profile smooth during sailing [52, 53]. These compounds showed serious sub-lethal due to releasing of low concentration, and they disrupt the endocrine leading to a sexual disorder of *oyster* [15]. These compound attached on mammal and weakened the immunological defense in fishes was reported by IMO and globally banned the application of TBT SPC on all vessels on 1 January 2003, as shown in Fig. 2 [67, 68].

Copper-based tin-free antifouling paint has subjected to environmental restriction due to a higher release rate; therefore, copper-based paint has been under scrutiny in several countries. Copper-based coating showed high toxicity to target organisms but common algae attached to the copper surface. Therefore booster biocide (diuron, irgarol 1051) was added in copper antifouling, showing highly biocidal coating and overcoming these problems [69], whereas copper-based paint is under the legislation of different countries to regulate the implementation of application due to lower toxicity [70, 71]. Therefore studies have been developed to control the release of the biocidal compound for a sustainable environment.

Controlled biocide-release antifouling coatings

The main idea of controlled-biocide-release based methodologies for AF coatings is to provide desired functionality at the surface. The three main strategies followed within this approach are hydrophilic, hydrophobic, and biodegradable based antifouling coating. In the upcoming section, we describe the most recent reported works for these principals and the strategies behind it. Biocides add to the original formulation, which is an effective antifouling strategy with far reduced aquatic contamination due to the slow release rate.

Hydrophilic antifouling coating

It is a big challenge for the antifouling technology because sea organisms adhered to the surfaces with different mechanisms due to the secretion of adhesive and forms conditioning film on the surface, as described in the below section. For this purpose, it is necessary to develop marine antifouling coating, which is applicable for the whole adhesive organism so that it may be possible for preventing adhesion of protein and bio-film [72]. Hydrophilic compounds with biocide have widely used for this purpose in marine applications.

For instance, Abiraman et al. [73], synthesized chitosan capped copper oxide nano leaves (CCCO NLs) by ultrasound sonication which was used as antifoulant and further it was mixed with commercial polyurethane paint. The surface of the antifoulant was smooth and homogenous in comparison to the uncoated panel, as shown in Fig. 3A. When chitosan content increased in the composite, it enhanced the hydrophilicity of

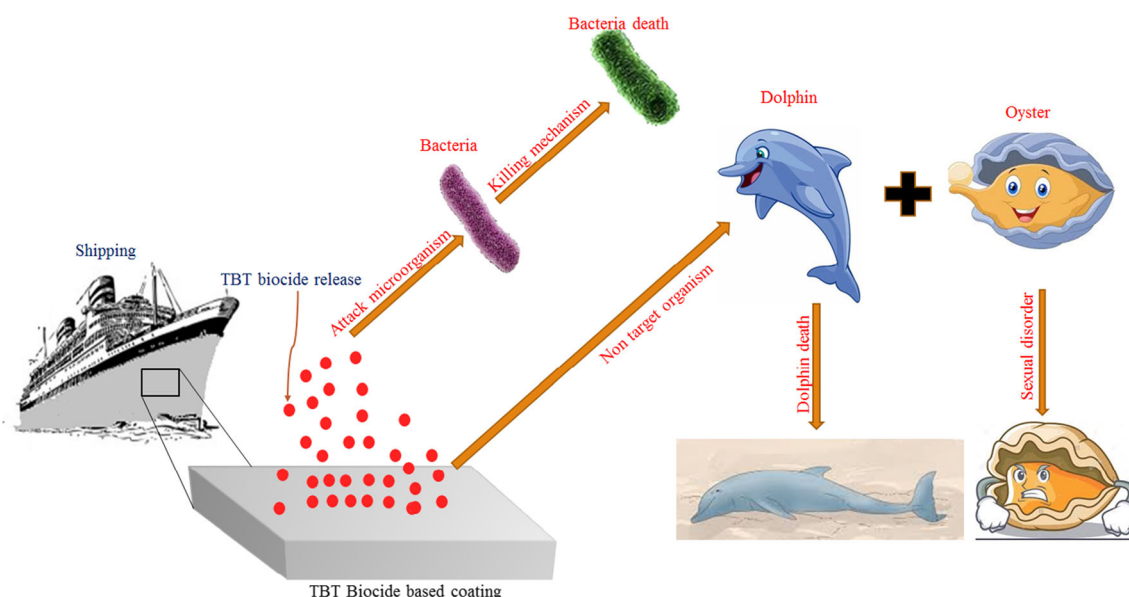


Fig. 2 killing mechanism of TBT based antifouling coating through their toxic effect [60]

antifoulant because chitosan is hydrophilic. The hydrophilicity of antifoulant increased on the surface, so it decreased the algae growth on the surface for 30 days in artificial seawater (ASW), as shown in Fig. 3B. Moreover, the adhesion strength of the antifoulant containing topcoat to the substrate was high because the base coat increased the binding efficiency between the panel surface and antifoulant. Therefore, it prevented the leaching of CCCO NLs from the surface of the panel.

In a related study, it was also decorated chitosan on the surface of the copper nanoparticles (NPs) [74]. The size of Cu NPs was 2 nm which was confirmed by a Field emission scanning electron microscope (FESEM), while chitosan decorated copper nanoparticles (CDC NPs) coated panel surfaces were homogeneous and very smooth, confirmed by atomic

force microscopy (AFM). CDC NPs used as antifoulant; therefore, it was mix with commercial polyurethane paint and showed good antifouling activity without releasing for 30 days, as shown in Fig. 3C.

Recently, Al Naamani et al. [75], synthesized chitosan/ZnO hybrid coating, which showed antifouling activity in mesocosm study under tank consisting seawater and controlled laboratory for four weeks. Their result showed that chitosan/ZnO as antibacterial activity (*Pseudoalteromonas nigrifaciens*), and anti-diatom (*Navicula sp*) in comparison to chitosan demonstrated by flow cytometry as shown in Fig. 3D. The incorporation of ZnO with chitosan demonstrated for coating application was a promising strategy for preventing the growth of marine microorganisms on the wetted surface. Similarly, it found that chitosan adorned ZnO

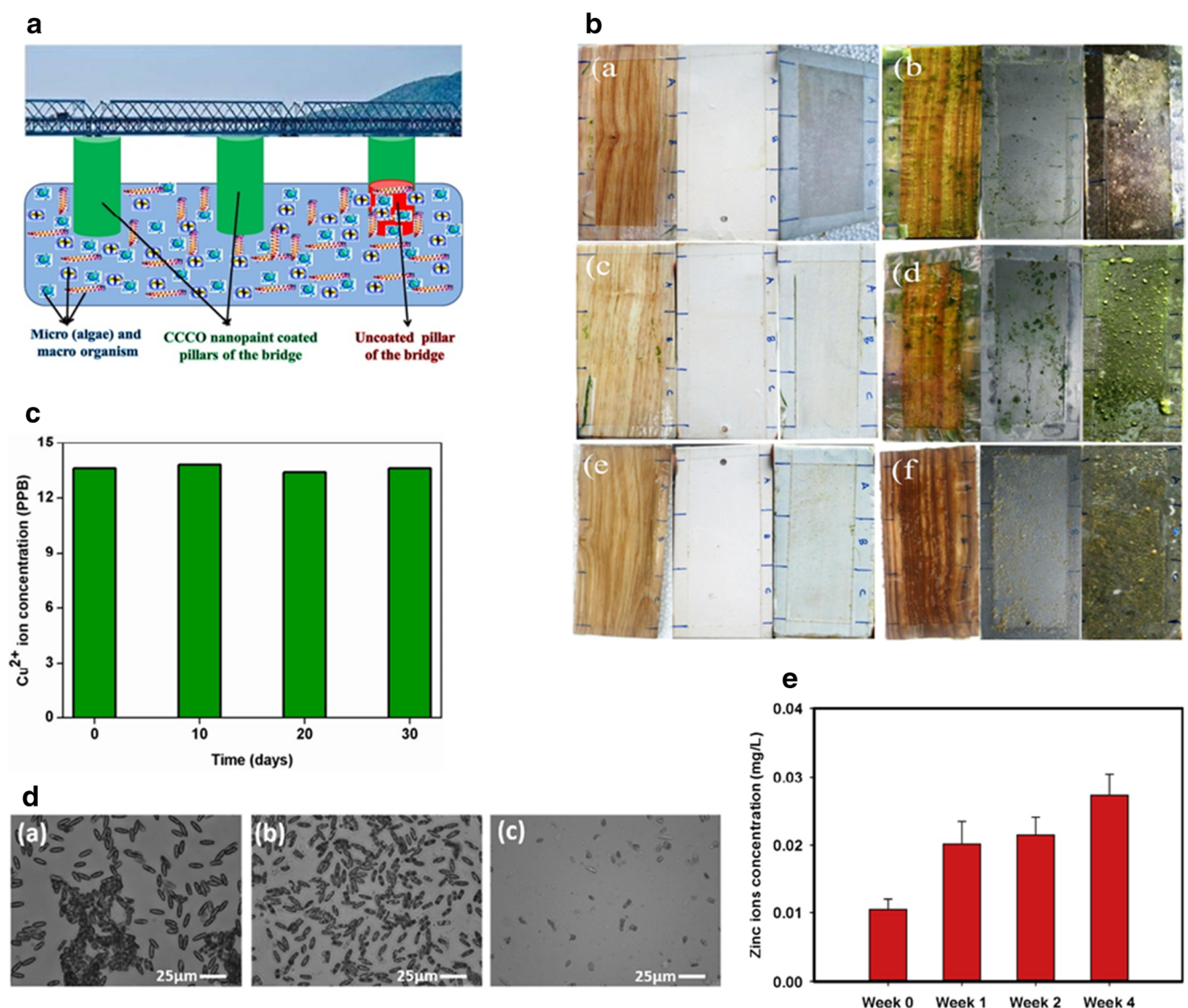


Fig. 3 a Schematic illustration of chitosan capped copper oxide nano leaves coated and the uncoated panel. b After algal treatment of CCCO nanopaint (a,c,e) coated and (b,d,f) uncoated panels [73]. c Concentration of Cu^{+2} ion in water [74]. d Diatom observation of (a) control, (b)

chitosan coating, and (c) chitosan/ZnO nanocomposite coating after incubation under fluorescence microscope for 7 days. e The releasing rate of Zn ion from Chitosan/ZnO composite [76]

showed excellent antifouling efficiency against algae due to hydrophilicity in both fresh and seawater for 30 days without toxic effect on the environment, as shown in Fig. 3E [76].

Recently, Vadana et al. [77], found biofilm formation on the surface of polyurethane during the observation, and made further improvement in this area by modifying PU with 1 to 2% Polyaniline-ZnO (PANI-ZnO) nanocomposite. Thus 2% ZnO used as filler influenced the increased order of PANI and also increased crystallinity. Therefore, the high crystallinity and hydrogen bonding had increased the higher tensile strength with good mechanical young's modulus as compared to PU film, as shown in Fig. 4A. The incorporation of PANI-ZnO (PNZ) nanocomposites filler in the PU improved hydrophilicity and wetting processes, resulting in a significant reduction in biofilm on the surface compared with PU, as shown in Fig. 4B.

Moreover, Adelung et al. [78], synthesized nano and microscale 0.1 to 5% tetrapod Zinc oxide (t-ZnO) by the flame transport synthesis (FTS), and particles incorporated as filler in the polythiourethane (PTU) coating. The composite containing 5%wt ZnO showed an increase in adhesive strength between the composite and substrate through moulding mechanism. It also showed higher hydrophilicity as compared to PTU. Therefore, 5% t-ZnO composite showed excellent antifouling activity than PTU and 1% t-ZnO-PTU in the seawater, as shown in Fig. 4C. Although hydrogels are made up of hydrophilic polymer because they contain 80% water, they are also highly elastic and resistant to non-toxic proteins. Polyethylene glycol (PEG) is strongly hydrophilic, charged neutrally and non-toxic, whereas PEG with transition metal has shown stronger antifouling [79, 80]. For this reason, ZnO

NPs and aminobenzoic agarose polymer network structure modified PEG methyl ethyl methacrylate and exhibited excellent AF properties with negligible cytotoxicity. Such hydrogels showed excellent protein resistance, bacterial attachment, and cell cohesion, thus showing high antifouling activity [81, 82]. The sol-gel process can be utilized to develop an environmentally friendly antifouling system based on biocide hybrid because it is a mature platform for the development of marine coating for hydrodynamic properties of ships and prevention of biofouling. Krupa and Vimala et al. synthesized ZnO particle using endosperm of coconut oil then further modified tetraethoxysilane (TEOS) sol-gel by doping, which showed antifouling and potentially evaluated at laboratory scale experiment, and the different volumes of liquid sol-gel coated and cured under various conditions. While ZnO NP doped with TEOS sol-gel exhibited the highest biofilm inhibition of 89.2% in comparison to undoped sol-gel [83].

Hydrophobic antifouling coating

The surface energy is described in the thermodynamically homogeneous interior of a material or coating as the excess energy of the molecules on the surface. The surface energy can be measured by calculating the contact angle using different liquids. Although a lower surface energy usually means less ability to interact with other compounds and materials spontaneously [84].

Hydrophobic coating is composed of fluorine and silicone, while both have higher contact angle and lowest surface energy. Therefore, they release or remove the attached

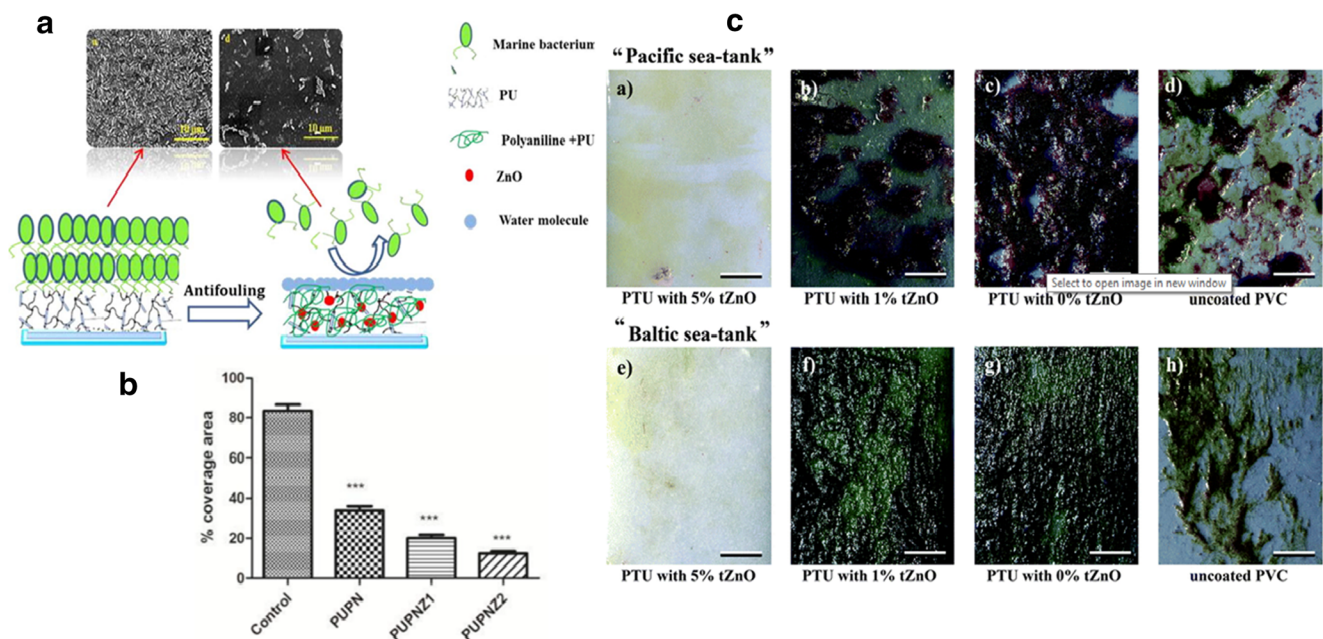


Fig. 4 **a** The percentage of the covered area by biofouling from the different samples after immersion in seawater, **b** The schematic illustration of the Polyaniline-Zinc oxide (PANI-ZnO) nanocomposites [77]. **c** Coating surface of the PTU-t ZnO after immersion in seawater for 30 weeks [78]

biofouling on the surface through direct cleaning and ship speed through the water. The development of advanced materials, particularly the useful hybrid nanocomposite, has become an essential need to ensure improved and frequently physical characteristics at a decreased cost. Mixture inorganic-organic nanocomposite gives the chance to combine the properties of two materials and create innovative materials. The dispersion of biocide nanoparticle in polymer enhances the self-cleaning performance, anticorrosive, and AF performance. Furthermore, the silicone-based FR coating reduces the interaction of fouling attachment on the surface and also remove the attached fouling back to the sea without releasing biocide.

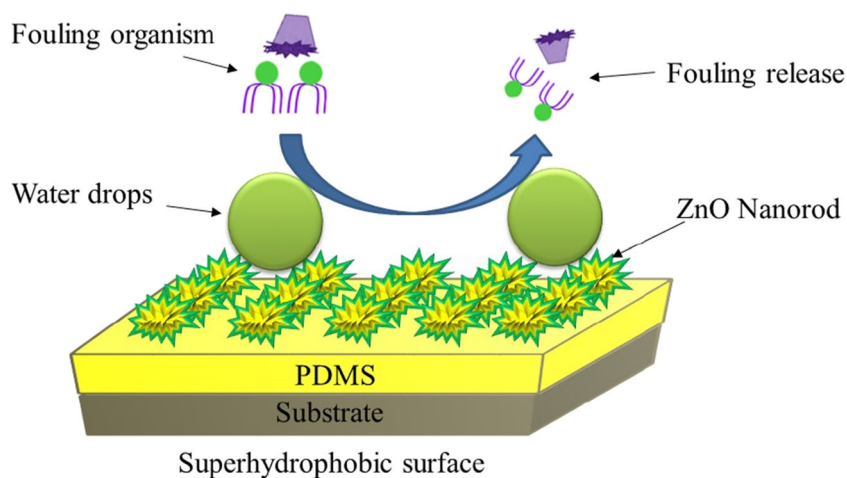
For this purpose, metal oxide NPs Cu_2O exhibited distinct bactericidal activities caused by their chemical properties. Selim et al. [85], investigated that silicon filled (different content 0.1 to 5% Cu) nanocomposite showed eco-friendly antifouling coating, while Polydimethylsiloxane(PDMS/0.1% Cu nanocomposite showed excellent efficiency due to complete deagglomeration and dispersion, which improved wettability, hydrophobicity and surface roughness. Therefore, PDMS/0.1% Cu enhanced the fouling release effect. Therefore, PDMS 0.1% Cu showed good antifouling ability (*yeast, Gram-positive and Gram-negative bacteria*) for 30 days in water and controlled release of biocide.

In another study of Jiang *et al.* [86], reported that Copper nanowire (CuNW) exhibited antibacterial and antifouling properties; therefore, CuNW was used as biocide in polymer for fouling release coating. For this purpose, CuNW was embedded in the elastomeric PDMS with different content from 12.5 to 250 $\mu\text{g}/\text{cm}$. While the PDMS containing 25 or 12.5 $\mu\text{g}/\text{cm}$ CuNW in comparison to control PDMS, which indicates the amount of CuNW had excellent antifouling performances against cyprid and had lower toxicity for nauplii than cyprid after 50 days. While these organisms did not significantly effect on PDMS film after 50 days because the embedded CuNW in the PDMS maintained their morphology, which was confirmed by TEM. CuNW interconnected with PDMS allowed the copper ions to continuously diffuse out from matrix in seawater. But Film controlled the release of copper ions and showed an excellent effect on marine biofouling for a long period. Arukram et al. [87] prepared a perfluorodecyl trichlorosilane (FDTS)-based PDMS-ZnO exhibited low adhesive strength, antifouling, and anticorrosion properties on steel Q235. The FDTS modified PDMS-ZnO showed an excellent corrosion resistance compared to unmodified PDMS-ZnO on steel Q235 in 3.5% NaCl, which was demonstrated by EIS. However, the presence of FDTS improved the alteration barrier behavior of the hydrophobic coating. Marceaux et al. [88], developed polyorganosilazane(PSZ)film, which showed flexibility, hydrophobicity, and adhesion property. Furthermore, they prepared different coating with Cu_2O . The PSZ containing Cu_2O exhibited excellent fouling after

17 months in seawater as compared with bare and reference coating, but this composite exhibited antifouling/anticorrosion potential without the release of Cu_2O . Several nanocomposites possessed superhydrophobic characteristics with metal oxide, i.e., CA of more than 150° , which increased the performance of coatings of ship hulls. Sanker et al. [89], reported that CuO - Cetyltrimethyl ammonium bromide(CTAB)incorporated in PDMS showed good antifouling activity against most bacterial and diatom due to the nanofiller dispersion, surface roughness, and hydrophobicity. Therefore, the performance of the antifouling was significantly excellent as compared to bare stainless steel and unmodified PDMS. While fewer shells found on the surface for 45 days in seawater; thus, the incorporation of ZnO in the matrix improved the antifouling behavior, and so it reduced the barnacles fouled on the surface. Selim et al. [90], reported that (0.5% to 5%) filler zinc oxide nanorod (ZnO NR) in silicon enhanced non-wettability and foul release coat. Because the distribution of ZnO 0.5% was excellent in silicon material because of roughness, indicated by FESEM. In addition to 0.5%, nanofiller reflected super-hydrophobicity due to the rough topographical structure of nanocomposite. Therefore, Silicon/0.5% ZnO NR showed elasticity, self-cleaning, and durability. Silicon/0.5% ZnO NR composite also showed higher prevention of various bacteria and fungi as compared with bare and silicon rod for 6 months in natural seawater due to super-hydrophobicity and homogenous roughness, as shown in Fig. 5. This finding was related to the high mobility on the slippery interfaces and the low surface energy of the interfused liquid. Zhang et al. [91], prepared ZnO /PDMS composite showed oil fouling resistance. The composite showed super-hydrophobicity with super oleophilic properties, while nanostructure of morphology was confirmed by SEM. ZnO/PDMS showed the 160° water contact angle; as a result, ZnO/PDMS exhibited excellent antifouling behavior with oil-absorbing on the substrate due to swelling, because composite was swelling due to PDMS. In this study, ZnO containing pure boron carbon-nitrogen sheet dispersed in PDMS, so it formed a durable coating on aluminum alloy with high hydrophobicity; therefore, it showed self-cleaning and oil fouling resistant [92]. In addition, there are many more examples of FRC modification summarized in the number of published reviews [60, 93, 94].

These results indicated that a microencapsulated biocide adds to the first formulation to be released slowly and promises effective antifouling with significantly reduced ocean pollution. Before the implementation of the above invention the incorporation of biocides into PDMSE networks was not feasible, because a single low volume of biocides could be used in a silicone coating to preserve surface smoothness due to a significant degree of immiscibility with the composition of the matrix, and the biocides could be released rapidly from the silicone matrix (due to high water solubility).

Fig. 5 The incorporation of ZnO nanorod with PDMS prevents fouling adhesion [90]



Biodegradable antifouling coating

Biodegradation is mainly concerned with biodegradable polymers while the metabolic action of microorganism involved in the primary degradation. The dynamic surface refers to a changing surface that continually renews itself in seawater and therefore decreases biofouling adhesion [95, 96]. The researcher developed dynamic surface coating based on this strategy by polyester-polyurethane, modified based degradable polyester and polyester-acrylate-based biodegradable polymer in marine antifouling coating. Such biodegradable polymers used as binders that controlled the release rate of eco-friendly antifoulants, and showed excellent antifouling behavior with tunable renewability [38, 97].

Mechanism

The main mechanism for the release of antifoulant is biodegradation and erosion. A loss of molecular weight characterizes deterioration and induces polymer erosion. Polymer degradation accompanied by a change in properties like tensile strength, color, shape, etc. Because polymer under the influence of one or more environmental factors such as heat, light or chemicals [35, 98]. The polymer surface can reduce the time of contact between the organism and the substrate, making their interaction similar to a non-adhesive impact, thus reducing the interaction strength with fouling organism, as shown in Fig. 6. The processes of physical erosion can be represented as heterogeneous or homogeneous. The polymer erodes only on the surface in heterogeneous erosion, also called surface erosion, and retains its physical integrity as it degrades. Most polymers undergo homogeneous erosion, meaning that hydrolysis occurs uniformly throughout the polymer matrix. Such polymers appear to be more hydrophobic in general [99, 100].

There are many mechanisms for degradation, such as mechanism I, II, and III. Cross-linked water-soluble macromolecules are prospective to form a three-dimensional network in mechanism I. In mechanism II, water-insoluble macromolecules with side groups converted into water-soluble polymers are dissolved as a result of ionization, protonation, and hydrolysis of the macromolecules. These polymers are soluble by carboxylic group ionization. The insoluble polymers with labile bonds follow Mechanism III. Hydrolysis of labile bonds results in splitting of the polymer backbone, forming water-soluble molecules of low molecular weight [101].

The polymer mechanism has been further proved by observing the settlement of model microfoulers on the surfaces of degradable polymers [102, 103]. The effect of the degradation rate on the near-surface motion of bacteria strains *Pseudomonas sp* and *Escherichia coli* (*E. coli*) was observed.

Model surfaces are developed using a DEM isomer of PCL, as a part of copolymerization to change the rate of PCL degradation. QCM-D tests showed that with DEM

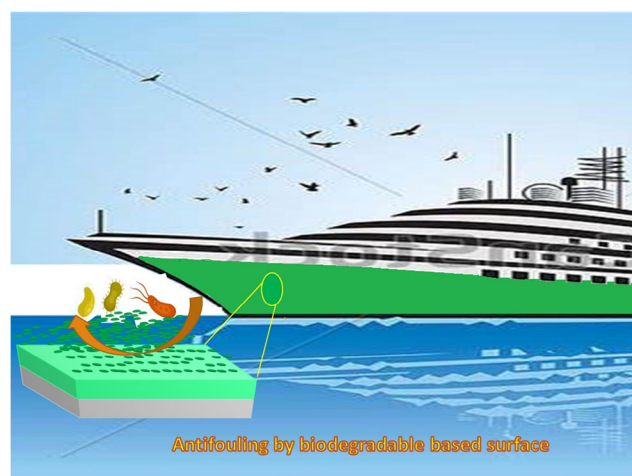


Fig. 6 The schematic illustration of antibiofouling by biodegradable polymer

content, the enzymatic level of degradation increased distinctly. In addition, the copolymers shape surfaces of similar roughness and wettability, thereby reducing their effects as well. The effect of the degradation rate on bacterial adherence can be extracted. The coverage of each bacterial strain on a poly surface decreased by the rate of degradation increases [104, 105]. Polymer degradation created a changing dynamic surface that prevented permanent bacterial adhesion due to reduced adhesion strength. Such results clearly showed that the complex surface alters bacteria's movement in a manner that facilitated their detachment and surface escape. The biodegradable polymer process occurs throughout the seawater immersion because there is always hydrolytic and enzymatic degradation [97].

On the other hand, biodegradable polymers may undergo enzymatic and hydrolytic backbone cleavage, resulting in oligomers or small molecules that ultimately become carbon dioxide and water after a certain period. Even for polymers containing degradable and non-degradable parts, the degraded material is much smaller particles and therefore has no negative environmental impact.

Poly-urethane based biodegradable antifouling coating

Polyurethane was fabricated by the condensation between polyisocyanate and polyol of the polymerization reaction [38]. While ester group of the polyester showed degradation and enzymatic degradation by the main chain led to a renewable surface and showed good antifouling coating, but traditional polyester polylactic acid (PLA), polycaprolactone (PCL) and polybutylene succinate (PBS) had high crystallinity and weak adhesion strength to the substrate and quite slow-releasing rate [106, 107]. Although, they can be improved by blending or modify with a polymer to control the release rate of the antifoulant for marine antifouling coating.

It has been reported that Poly(ethylene-adipate) (PEA), or poly(1,4-butylene adipate) (PBA) or poly(1,6-hexamethylene adipate) (PHA) with the polyurethane were degraded in the presence of ester density and showed an excellent adhesion [108]. The mass loss of PHA-PU, PBA-PU, and PEA-PU were about 0.40, 0.75, and 0.80 mg/cm for 2 months immersion in ASW, respectively. But the mass loss of polymer increased with ester density, because there was the available number of main chain cleavage. The degradable polyurethane had excellent adhesion to the substrate over 4 MPa due to strong interaction with the polymer, so it formed a hydrogen bond, which was efficient for long time antifouling applications in seawater, as shown in Fig. 7A. Furthermore, the researchers had been prepared different degradable polyurethane with diol polyesters such as polypropylene glycol-CL-LA

and star-shaped [39, 109]. Ma et al. [110], synthesized CL-PU in which PCL acted as a soft segment with polyurethane as a hard segment, whereas the presence of PCL in the PU show higher crystallinity and lower hydrolytic degradation. Therefore, CL-PU was modified with glycolide (GA) as a soft segment by ring open polymerization. The CL/GA-PU showed a lower crystallinity than CL-PU confirmed by DSC, because GA was reduced the crystallinity and destroyed the polymer chain regularity and increased the amorphous region. Therefore, the water molecule attacked the ester bond in the polymer due to the presence of an amorphous region. The hydrolytic and enzymatic degradation performance of CL/GA-PU increased with an increased in GA contents from 0 to 10%, as shown in Fig. 7B. The CL/GA-PU exhibited good antifouling activity in the seawater for 150 days. However, the small amount of fouling appeared on the lower surface of CL/GA-PU after 150 days, as shown in Fig. 7C. The hydrolysis group in the polyurethane had improved the biodegradability. The PCL-PU grafted with TIPSA to yield a degradable main chain and hydrolyzable side chain. The poly triisopropylsilyl acrylate (PTIPSA) content influenced the mass-loss rate in the ASW. The TIPSA content increased in the polymer, so it also increased the mass loss of composite from 0.1 to 3.5 wt% day. The mass loss slightly changed on the surface morphology due to side-chain hydrolysis and main chain degradation. Owing to the surface roughness was slightly varied with time, while 40 wt% PTIPSA content polymer composite showed higher enzymatic degradation and antifouling performance for 3 months in seawater [111]. The degradable polyurethane grafted with hydrolyzable PTIPSA, so the density of the ester group and mass loss depend on the consistent of the PTIPSA because the higher mass loss due to the higher molar mass of the PTIPSA. Hence, the long side chain of PTIPSA increased the ester group density for hydrolysis. It had also reported the grafting of the side group N-(2,4,6-trichlorophenyl) maleimide (TCPM) moieties acted as antifoulant with PCL-PU [112]. The TCPM decreased the spherulite size of PCL as a soft segment. Hence, the content of TCPM was above 30%, so the phenyl group of TCPM prevented the increasing of spherulite and polymer had become amorphous. The TCPM had also increased the enzymatic degradation rate in ASW due to the amorphous parts and increased the fouling resistance activity of PCL-PU to marine biofouling. The polymer exhibited excellent antifouling activity and surface renewal, as shown in Fig. 7D. But in the marine field, the biodegradable polymer had been used as a carrier of antifoulant and also controlled the release rate of antifoulant [33, 113, 114].

The release of antifoulant 4,5-dichloro-2-octylisothiazolinone (DCOIT) from PHA/PEA/PBA based polyurethane and its extraction settle down, while the cumulative

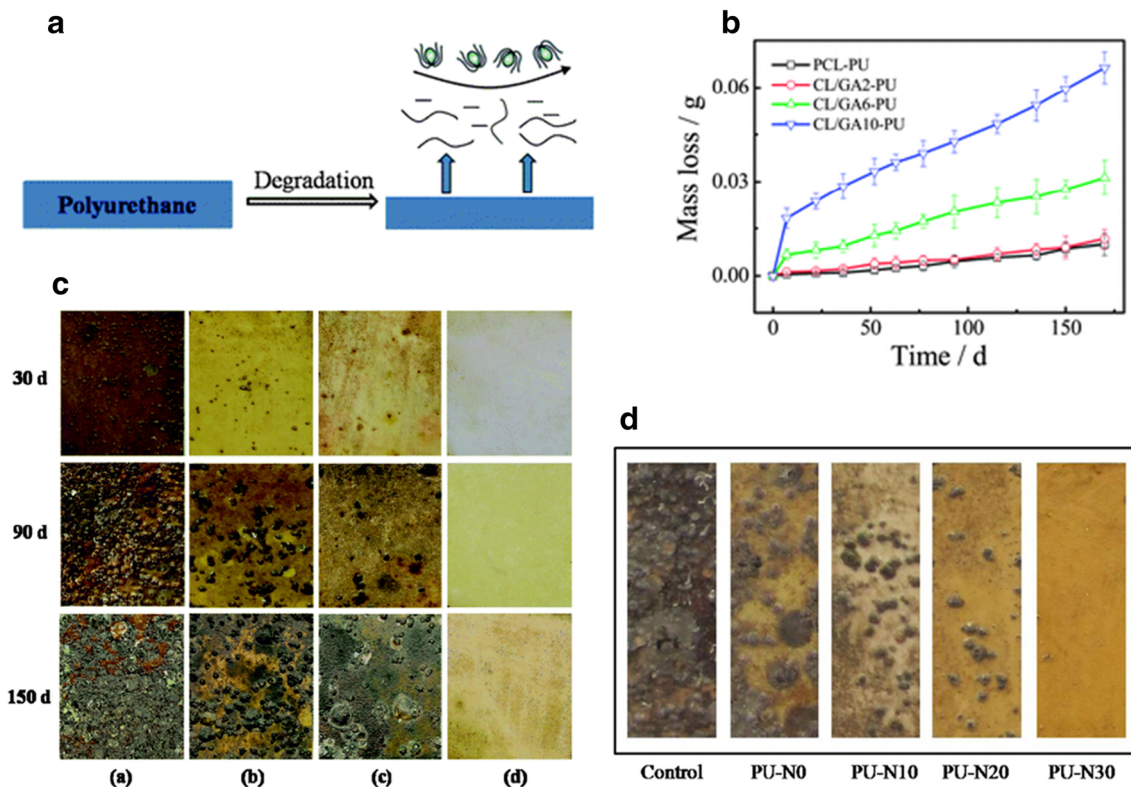


Fig. 7 **a** The schematic release of antifoulant from degradable polyurethane [108] **(b)** The time dependence on the mass loss CL/GA-PU and, **(c)** Coating surface on the CL/GA-PU after immersion [110]. **d** Coating surface on the degradable polyurethane after immersion for two months [112]

release of DCOIT increases linearly to correlate with coefficient > 0.99 , which was demonstrated by UV spectrophotometer. Therefore, the coating showed excellent antifouling activity for 6 months in the seawater, and it also showed a self-renewal surface. In another degradable and hydrolyzable.

polyurethane polymer, the release rate of the DCOIT became stable with time. When increased mass loss of polymer also increased the release rate, while the degradation polymer controlled the release rate of antifoulant [108]. In another study of star-shaped polyurethane, the release rate of the copper ion observed was steady in 31 days and showed excellent antifouling coating performance in seawater immersion for 50 days [109].

As we know that biodegradable polymer gradually erodes and decomposed in the seawater while degradable polymer itself leads to a self-renewal surface. As a result, the higher degradation rate led to a short period. This information is applicable in the marine antifouling coating, which is given above so, we can suggest that antifoulant can be used in the durable antifouling coating. While antifoulant has quick-release rate in the initial stage in water but the release rate gradually decreases with the period. The degradable polyurethane is a suitable binder for carrying antifoulant because its surface becomes renewal in water and release the antifoulant with stable condition.

Modified polyester based biodegradable antifouling coating

The biodegradability of polyester could be improved by the modification of polyester because the crystallinity of polyester becomes reduced and degradation increases lead to suitable antifouling, self-renewal, and carrier for antifoulant.

It had been reported that in the fabrication of PCL/Clay composite, the clay decreased the spherulite size of the PCL confirmed by polarizing optical microscope (POM) [115]. But crystallinity of clay was close to PCL demonstrated by differential scanning calorimetry (DSC). The clay reduced the spherulite size as increased the amorphous region and improved the penetration of water with composite. Therefore, the PCL/clay showed faster hydrolytic and enzymatic degradation. Whereas the DCOIT as antifoulant incorporated into the PCL/clay-composite, so it carried the DCOIT and gradually released into the seawater, as shown in Fig. 8A. The composite exhibited antifouling activity for 10 months in seawater. However, clay did not reduce the large spherulite size after a long period, so it was affected on the composite and reduced the mechanical property and resulted in raising some cracks on the surface. The blending of polyester was also found to be significant for antifouling activity. Poly(ϵ -caprolactone) (PCL) and Poly(butylene succinate) (PBS) was prepared by the blending of the PCL and PBS [116].

The composite showed lower crystallinity because PBS was decreased the spherulite size of the PCL and increased the amorphous interfacial area in the composite. The 70/30 PCL/PBS containing composite exhibited higher mass loss for 120 days in ASW, as shown in Fig. 8B. The composite was also used as a carrier of DCOIT, while DCOIT distributed uniformly in the composite due to the constant release rate observed in ASW. Contrary, the constant release rate of DCOIT was linear time to correlate coefficient < 99. The composite with DCOIT had excellent anti-biofouling activity, so the growth of biofouling was restricted on the composite for 120 days, as shown in Fig. 8C. Polyester was also chemically modified for anti-biofouling purposes.

Fay et al. [117], synthesized polyester block with anhydride by a melt condensation reaction, in which polymer composite used as a carrier of antifoulant (Diuron). The copolymer enabled to inhibition of adhesion of microalgae and bacteria in the marine field, as shown in Fig. 8D. However, the polymer

coating completely degraded due to the presence of anhydride block for 10 months in the seawater. Fay et al. [118], copolymerized CL with L-lactide (LA) and valerolactone (VL). The crystallinity of composites was lower than each polymer; therefore, they showed good degradability while composite used as a binder for carrying antifoulant in the paint. The binder showed good hydrolytic degradation, but antifouling activity is not reported in seawater. It was further prepared CL with LA and VL, which showed good hydrolytic degradation and antifouling activity for 3 months in seawater, which was demonstrated by SEM [119]. It had also investigated that copolymerization of CL and VL could be used as a binder for carrying antifoulant (Copper thiocyanate, Zinc pyritone) in the paint. The binder resulted in good hydration, erosion, degradation, and biocide release. The binder containing paint showed excellent anti-macrofouling activity for more than one year as compared to commercial paint [120]. Azmar et al. [121], synthesized the triblock polymer, which

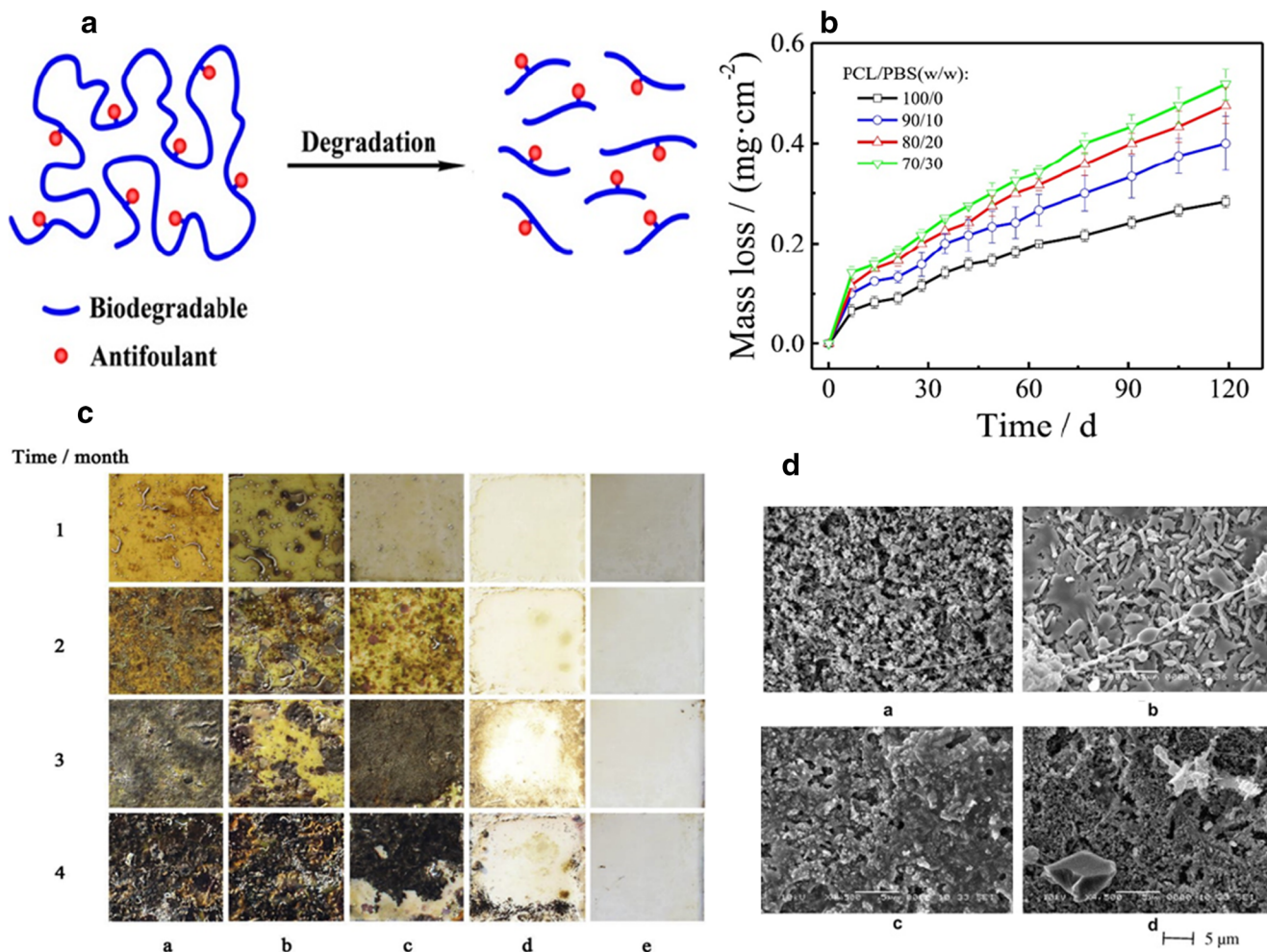


Fig. 8 a The schematic release of antifoulant from PCL-Clay [115]. b The time shift Time dependence of mass loss of PCL/PBS, and (c) Coating surface on the PCL/PBS after immersion in seawater for 120 days [116]. (d) Colonization observation of (A) poly(methylmethacrylate-co-

butylmethacrylate) PMMA-PBMA paint; (B) TBT paint; (C) paint without antifouling activity; (D) polyester block with anhydride paint after immersion of 3 weeks in seawater [117]

Fig. 9 **a** Schematic illustration of MDO-TBSM-MMA via RROP [122]. **b** Schematic illustration of MDO-methyl silyl methacrylate copolymer [123]. **c** Schematic illustration of MDO-MMA via PROP [124]

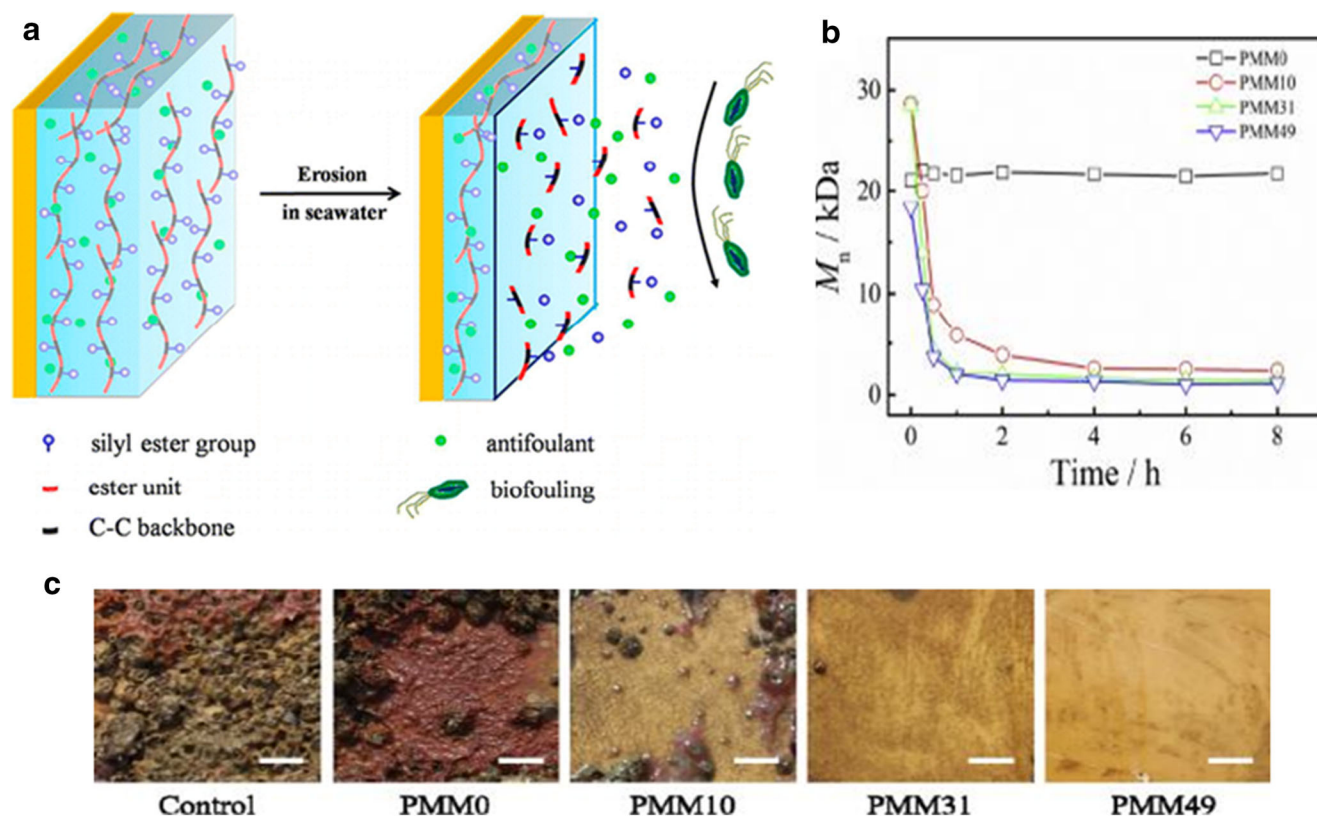
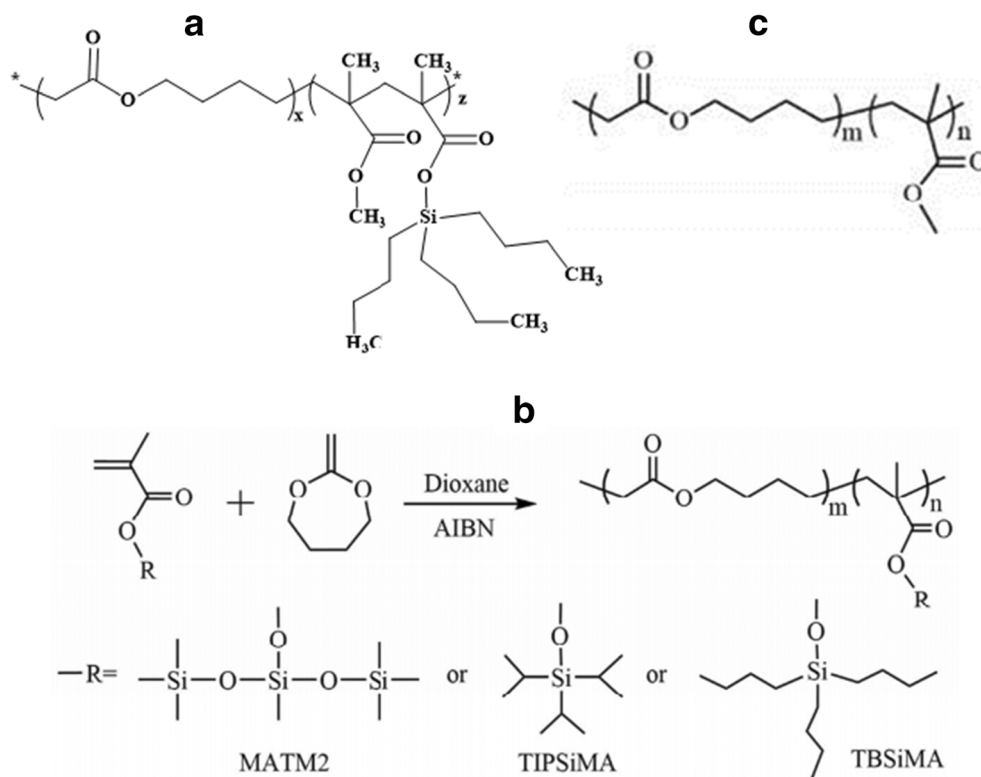


Fig. 10 **a** The schematic release of antifoulant from MDO-Silyl methacrylate [122]. **b** The time dependence of the molar mass of the MDO-MMA copolymer in 0.1 M KOH solution [124]. **c** Coating surface on the copolymer after immersion in seawater for 90 days [124]

showed hydrophobicity and degradability. The copolymer was mixed with antifoulants (Dichlofluanide, zinc pyrithione, and copper thiocyanate) to prepare the coating. Triblock copolymer used as a binder in the coating, which was not only decreased the crystallinity, and also improved the degradation due to the presence of PDMS. While the adhesion strength of modified polyester was normally poor than polyester-based polyurethane due to lack of adhesive moieties and high crystallinity, because it was obtained from copolymerization, or physically blending. Therefore there were often cracks raised on the coating surface.

Polyester acrylate-based biodegradable antifouling coating

Traditional SPC binder improved the surface erosion and showed the antifouling application statically; therefore, degradable SPC developed with a biodegradable polymer. For this purpose, Zhou et al. [122], prepared polyester by copolymerization of 2-methylene-1,3-dioxepane (MDO), trimethylsilyl methacrylate (TBSM) and methylmethacrylate (MMA) by PROP, as shown in Fig. 9A. The degradable main chain improved the erosion of TBSM and avoided swelling; therefore, a copolymer containing 23% polyester showed 13% mass loss and 30% water absorption in ASW. While TBSM with polymer showed 5% mass loss and 77% water absorption, which was efficient for low speed, as the copolymer was used as a carrier of antifoulant so that the release rate has remained stable. The coating showed good antifouling activity during static conditions while the copolymer which did not have MDO swelled and showed weak antifouling activity, as shown in Fig. 10A.

Similarly, Bressy et al. [123], copolymerized MDO with triisopropylsilyl methacrylate (TIPSM) and bis (trimethylsilyl methacrylate (MATM2) as shown in Fig. 9B. When the hydrolysis ester increased, its steric hindrance decreased. MDO-MATM2 and MDO-TIPSM showed lower mass loss by 90% and 86% at room temperature in ASW for 7 weeks due to the main chain, while mass loss increased at 60 °C. MDO and TIPSM did not show a significant effect with a molar mass of the polymer on room temperature and 60 °C. While silyl ester rapidly hydrolysis hence carboxyl group generate and gave highly water absorption, so these factors influence the degradation. While silyl acrylate was a good one as the binder for zinc and copper because zinc/Cu based SPC widely used for the antifouling activity. Recently, Dai et al. [124], prepared copolymer with MDO and MMA by PROP, as shown in Fig. 9C. The MMA moieties had good adhesive rate; therefore, copolymer showed excellent adhesion to the

substrate and amorphous region. The copolymer showed rapidly decreased molar mass in alkaline solution due to MDO, but it did not affect the MDO as shown in Fig. 10B. The hydrolytic and enzymatic degradation rate of copolymer increased due to the main chain ester. The copolymer also showed good carrier antifoulant (DECOIT) and controlled the release rate. When the copolymer containing higher content above 31% polyester, so it showed excellent antifouling ability for 3 months in the seawater as shown in Fig. 10C.

Conclusion and future prospects

In order to design high performance antifouling system, the presence of biocide nanocomposite plays a pivotal role on the influence of hydrophobicity/hydrophilicity. The biocide nanocomposite had a wide range of applications in marine industries and eco-friendly coating as an alternate to toxic antifouling coating, because of nanocomposite biocide release at a lower amount and show excellent antifouling performance through a hydrophilic and hydrophobic antifouling coating. Additionally, the different biodegradable antifouling coating has an efficient and auspicious strategy, because degradable polymer showed excellent mechanical properties, antifouling performance, and surface renewability with the degradable self-polishing copolymer. Besides, the framework of the biodegradable polymer in a mix with eco-friendly antifoulant has demonstrated durable antifouling activity and also controlled the release of antifoulant due to constant renewability of surface.

Complexities of biofouling organisms and marine conditions is a remarkable challenge to antifouling. Materials dependency on an antifouling mechanism barely fulfils the need for issues of various occasions. In future research, the design of antifouling materials should consolidate with various mechanisms. Wide range drag-decrease or fouling resistant moieties can be combined into degradable polymers to create multifunctional dynamic surfaces. Condition of versatile, unique surfaces with reaction to fouling weight, temperature, saltiness, and ship speed are another significant direction for changing service conditions. Besides, the biodegradable polymer can be prolonged with different materials for example, the fabrication of a significant polymer by the introduction of hydrolyzable bond of degradable polymer with silicone-based FRC surfaces, so the advantages of the two kinds of materials are attained simultaneously. The fabrication of green eco-friendly biocide can control the release rate based on the FRC- degradable polymer with excellent adhesion and longer shelf life with durable antifouling activity.

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References

- Krishnan S, Weinman CJ, Ober CK (2008) Advances in polymers for anti-biofouling surfaces. *J Mater Chem* 18:3405
- Chambers LD, Stokes KR, Walsh FC, Wood RJK (2006) Modern approaches to marine antifouling coatings. *Surf Coatings Technol* 201:3642–3652
- Demirel YK, Khorasanchi M, Turan O, Incecik A (2013) On the importance of antifouling coatings regarding ship resistance and powering. *Low Carbon Shipp Conf* 44:1–13
- Schultz MP, Bendick JA, Holm ER, Hertel WM (2011) Economic impact of biofouling on a naval surface ship. *Biofouling* 27:87–98
- Wei C, Zhang G, Zhang Q, Zhan X, Chen F (2016) Silicone oil-infused slippery surfaces based on sol-gel process-induced Nanocomposite coatings: a facile approach to highly stable bioinspired surface for biofouling resistance. *ACS Appl Mater Interfaces* 8:34810–34819
- Jiang J, Zhu J, Zhang Q, Zhan X, Chen F (2019) A shape recovery Zwitterionic bacterial cellulose aerogel with superior performances for water remediation. *Langmuir* 35:11959–11967
- Fu Y, Jiang J, Zhang Q et al (2017) Correction: robust liquid-repellent coatings based on polymer nanoparticles with excellent self-cleaning and antibacterial performances. *J Mater Chem A* 5: 1313–1313
- Ba M, Zhang Z, Qi Y (2017) The dispersion tolerance of micro / Nano particle in Polydimethylsiloxane and its influence on the properties of fouling release coatings based on Polydimethylsiloxane. *Coatings* 7:107. <https://doi.org/10.3390/coatings7070107>
- Miao BA, ZHANG, Zhan-ping QY (2017) Research Progress of silicone antifouling paints. *Surf Technol* 46:1–8
- Lotz BA, Group TC (2016) Marine Coatings : Making Sense of U . S . , State , and Local Mandates of Copper-Based Antifouling Regulations. 50–54
- Chen X, Zhang G, Zhang Q et al (2015) Preparation and performance of amphiphilic polyurethane copolymers with capsaicin-mimic and PEG moieties for protein resistance and antibacteria. *Ind Eng Chem Res* 54:3813–3820
- Kiil S, Dam-Johansen K, Weinell CE et al (2002) Dynamic simulations of a self-polishing antifouling paint exposed to seawater. *J Coatings Technol* 74:45–54
- Almeida E, Diamantino TC, de Sousa O (2007) Marine paints: the particular case of antifouling paints. *Prog Org Coatings* 59:2–20
- Alzieu C (2000) Environmental impact of TBT : the French experience. *Sci Total Environ* 258:99–102
- Kotrikla A (2009) Environmental management aspects for TBT antifouling wastes from the shipyards. *J Environ Manag* 90:77–85
- Cologer PCC (1991) Fouling control of navy surface ships. *Nav Eng J* 103:114–115
- Almond KM, Trombetta LD (2017) Copper pyrithione , a booster biocide , induces abnormal muscle and notochord architecture in zebra fish embryogenesis. *Ecotoxicology* 26:1–13
- Soroldoni S, Martins SE, Castro IB, Pinho GLL (2018) Potential ecotoxicity of metals leached from antifouling paint particles under different salinities. *Ecotoxicol Environ Saf* 148:447–452
- Soroldoni S, Abreu F, Castro ÍB, Duarte FA, Pinho GL (2017) Are antifouling paint particles a continuous source of toxic chemicals to the marine environment? *J Hazard Mater* 330:76–82
- Wan F, Pei X, Yu B et al (2012) Grafting polymer brushes on biomimetic structural surfaces for anti- algae fouling and foul release. *ACS Appl Mater Interfaces* 2:4557–4565
- Zhang Y, Wan Y, Shi Y et al (2016) Facile modification of thin-film composite nanofiltration membrane with silver nanoparticles for anti-biofouling. *J Polym Res* 23:1–9
- Nurioglu AG, Esteves a CC, De WG (2015) Coatings based on molecular structure Design for Marine Applications. *J Mater Chem B* 3:6547–6570
- Shan CAO, Jiadao W, Haosheng C, Darong C (2011) Progress of marine biofouling and antifouling technologies. *Chin Sci Bull* 56: 598–612
- Quigg A, Chin W, Chen C et al (2013) Direct and indirect toxic effects of engineered nanoparticles on algae: role of natural organic matter. *ACS Sustain Chem Eng* 1:686–702
- Jin B, Zhang G, Lian J et al (2019) Boron nitride nanosheet embedded bio-inspired wet adhesives with switchable adhesion and oxidation resistance. *J Mater Chem A* 7:12266–12275
- Mallakpour S, Khadem E (2015) Recent development in the synthesis of polymer nanocomposites based on nano-alumina. *Prog Polym Sci* 51:74–93
- Enayatzadeh M, Mohammadi T, Fallah N (2019) Influence of TiO₂ nanoparticles loading on permeability and antifouling properties of nanocomposite polymeric membranes: experimental and statistical analysis. *J Polym Res* 26:11–22
- Chen K, Zhou S, Wu L (2015) Self-healing underwater Superoleophobic and anti-biofouling coatings based on the assembly of hierarchical microgel spheres. *ACS Nano* 10:1386–1394
- Mujeeb Rahman P, Abdul Mujeeb VM, Muraleedharan K, Thomas SK (2018) Chitosan/nano ZnO composite films: enhanced mechanical, antimicrobial and dielectric properties. *Arab J Chem* 11:120–127
- Tamayo L, Azócar M, Kogan M, Riveros A, Páez M (2016) Copper-polymer nanocomposites: an excellent and cost-effective biocide for use on antibacterial surfaces. *Mater Sci Eng C* 69: 1391–1409
- Ciriminna R, Bright FV, Pagliaro M (2015) Ecofriendly antifouling marine coatings. *ACS Sustain Chem Eng* 3:559–565
- Harder P-YQ, CKL-UDD S (2007) Marine biofilms as mediators of colonization by marine macroorganisms: implications for antifouling and aquaculture. *Mar Biotechnol* 9:399–410
- Ding W, Ma C, Zhang W, Chiang H, Tam C, Xu Y, Zhang G, Qian PY (2018) Anti-biofilm effect of a butenolide/polymer coating and metatranscriptomic analyses. *Biofouling* 34:111–122
- Faÿ F, Linossier I, Peron JJ et al (2007) Antifouling activity of marine paints: study of erosion. *Prog Org Coatings* 60:194–206
- Luckachan GE, Pillai CKS (2011) Biodegradable polymers- a review on recent trends and emerging perspectives. *J Polym Environ* 19:637–676
- Dobretsov S, Dahms HU, Qian PY (2006) Inhibition of biofouling by marine microorganisms and their metabolites. *Biofouling* 22: 43–54
- Cusick KD, Dale JR, Fitzgerald LA et al (2017) Adaptation to copper stress influences biofilm formation in *Alteromonas macleodii*. *Biofouling* 7014:1–15
- Chen Y, Liu Z, Han S et al (2016) Poly(propylene carbonate) polyurethane self-polishing coating for marine antifouling application. *J Appl Polym Sci* 133:1–9
- Yi J, Yi J, Ren R, Huang C (2015) Synthesis and characterization of degradable polyurethane based on poly (ether ester) polyols (PPG-2000 and ε -caprolactone / lactic acid) for marine antifouling. *J Coatings Technol Res* 12:525–532
- Xie Q, Pan J, Ma C, Zhang G (2019) Dynamic surface antifouling: mechanism and systems. *Soft Matter* 15:1087–1107
- Thompson SEM, Coates JC (2017) Surface sensing and stress-signalling in *Ulva* and fouling diatoms–potential targets for antifouling: a review. *Biofouling* 33:410–432
- Finlay JA (2006) The influence of surface wettability on the adhesion strength of settled spores of the green alga *Enteromorpha* and the diatom amphora. *Integr Comp Biol* 42:1116–1122

43. Frey M, Simard N, Robichaud D et al (2014) Fouling around: vessel sea-chests as a vector for the introduction and spread of aquatic invasive species. *Manag Biol Invasions* 5:21–30
44. Korkut E, Atlar M (2012) An experimental investigation of the effect of foul release coating application on performance, noise and cavitation characteristics of marine propellers. *Ocean Eng* 41:1–12
45. Lindholdt A, Dam-Johansen K, Olsen SM et al (2015) Effects of biofouling development on drag forces of hull coatings for ocean-going ships: a review. *J Coatings Technol Res* 12:415–444
46. Railkin AI (2004) Marine biofouling: colonization processes and defenses. CRC Press Taylor Fr Gr Boca Raton, Florida 3:320
47. Matranga V, Corsi I (2012) Toxic effects of engineered nanoparticles in the marine environment : model organisms and molecular approaches. *Mar Environ Res* 76:32–40
48. Stoodley P, Sauer K, Davies DG, Costerton JW (2002) Biofilms as complex differentiated communities. *Annu Rev Microbiol* 56: 187–209
49. Salta M, Wharton JA, Blache Y, Stokes KR, Briand JF (2013) Marine biofilms on artificial surfaces: structure and dynamics. *Environ Microbiol* 15:2879–2893
50. Kuliasha CA, Finlay JA, Franco SC, Clare AS, Stafslie SJ, Brennan AB (2017) Marine anti-biofouling efficacy of amphiphilic poly(coacrylate) grafted PDMS: effect of graft molecular weight. *Biofouling* 33:252–267
51. Bouyssou A (2013) The maritime commons : digital repository of the world biofouling : a means of aquatic species transfer
52. Callow JA, Callow ME (2011) Trends in the development of environmentally friendly fouling-resistant marine coatings. *Nat Commun* 2:210–244
53. Dafforn KA, Lewis JA, Johnston EL (2011) Antifouling strategies: history and regulation, ecological impacts and mitigation. *Mar Pollut Bull* 62:453–465
54. Compère C, Bellon-Fontaine MN, Bertrand P et al (2001) Kinetics of conditioning layer formation on stainless steel immersed in seawater. *Biofouling* 17:129–145
55. Hoa ND, El-Safty SA (2011) Synthesis of mesoporous NiO nanosheets for the detection of toxic NO₂ gas. *Chem - A Eur J* 17: 12896–12901. <https://doi.org/10.1002/chem.201101122>
56. Nguyen H, El-Safty SA (2011) Meso- and macroporous Co₃O₄ nanorods for effective VOC gas sensors. *J Phys Chem C* 115: 8466–8474
57. Dahlbäck B, Blanck H, Nydén M (2010) The challenge to find new sustainable antifouling approaches for shipping. *Coast Mar Sci* 34:212–215
58. Suman TY, Radhika Rajasree SR, Kirubakaran R (2015) Evaluation of zinc oxide nanoparticles toxicity on marine algae *Chlorella vulgaris* through flow cytometric, cytotoxicity and oxidative stress analysis. *Ecotoxicol Environ Saf* 113:23–30
59. Coutts ADM, Taylor MD (2004) A preliminary investigation of biosecurity risks associated with biofouling on merchant vessels in New Zealand. *New Zeal J Mar Freshw Res* 38:215–229
60. Selim MS, Shenashen MA, El-Safty SA et al (2017) Recent progress in marine foul-release polymeric nanocomposite coatings. *Prog Mater Sci* 87:1–32. <https://doi.org/10.1016/j.pmatsci.2017.02.001>
61. Yebra DM, Kiil S, Dam-Johansen K (2004) Antifouling technology - past, present and future steps towards efficient and environmentally friendly antifouling coatings. *Prog Org Coatings* 50:75–104
62. Kiil S, Weinell CE, Pedersen MS, Dam-Johansen K (2001) Analysis of self-polishing antifouling paints using rotary experiments and mathematical modeling. *Ind Eng Chem Res* 40:3906–3920
63. Champ MA (2000) A review of organotin regulatory strategies, pending actions, related costs and benefits. *Sci Total Environ* 258: 21–71
64. van der Geest HG, Booij P, Sjollem SB et al (2014) Hazard and risk of herbicides for marine microalgae. *Environ Pollut* 187:106–111
65. Yebra DM, Kiil S, Weinell CE, Dam-Johansen K (2006) Presence and effects of marine microbial biofilms on biocide-based antifouling paints. *Biofouling* 22:33–41
66. Rittschof D (2009) Trends in marine biofouling research. Woodhead Publishing Limited
67. Okoro HK, Fatoki OS, Adekola FA et al (2011) Sources, environmental levels and toxicity of organotin in marine environment - a review. *Asian J Chem* 23:473–482
68. Siedenbiedel F, Tiller JC (2012) Antimicrobial polymers in solution and on surfaces: overview and functional principles. *Polymers (Basel)* 4:46–71
69. Dahl B, Blanck H (1996) Toxic effects of the antifouling agent Irgarol 1051 on periphyton communities in coastal water microcosms. *Mar Pollut Bull* 32:342–350
70. Sapozhnikova Y, Wirth E, Schiff K, Fulton M (2013) Antifouling biocides in water and sediments from California marinas. *Mar Pollut Bull* 69:189–194
71. Blanck H, Eriksson KM, Grönvall F, Dahl B, Guijarro KM, Birgersson G, Kylin H (2009) A retrospective analysis of contamination and periphyton PICT patterns for the antifoulant irgarol 1051, around a small marina on the Swedish west coast. *Mar Pollut Bull* 58:230–237
72. Hong-lai GW, Ya-peng N, Han Xia L (2018) Dopamine-based poly(sulfobetaine methacrylate) surface modification and its antifouling properties. *Nat Sci Ed* 44:316–322
73. Abiraman T, Ramanathan E, Kavitha G, Rengasamy R, Balasubramanian S (2017) Synthesis of chitosan capped copper oxide nanoleaves using high intensity (30 kHz) ultrasound sonication and their application in antifouling coatings. *Ultrason Sonochem* 34:781–791
74. Abiraman T, Balasubramanian S (2017) Synthesis and characterization of large-scale (<2 nm) chitosan-decorated copper nanoparticles and their application in antifouling coating. *Ind Eng Chem Res* 56:1498–1508
75. Al-Naamani L, Dobretsov S, Dutta J, Burgess JG (2017) Chitosan-zinc oxide nanocomposite coatings for the prevention of marine biofouling. *Chemosphere* 168:408–417
76. Abiraman T, Kavitha G, Rengasamy R, Balasubramanian S (2016) Antifouling behavior of chitosan adorned zinc oxide nanorods. *RSC Adv* 6:69206–69217
77. Mooss VA, Hamza F, Zinjarde SS, Athawale AA (2018) Polyurethane films modified with polyaniline-zinc oxide nanocomposites for biofouling mitigation. *Chem Eng J* 359:1400–1410
78. Adelung R, Baum MJ (2016) Complex shaped ZnO nano- and microstructure based polymer composites : mechanically stable. *Phys Chem Chem Phys* 18:7114–7123
79. Li L, Chen S, Jiang S (2007) Protein interactions with oligo (ethylene glycol) (OEG) self- assembled monolayers : OEG stability, surface packing density and protein adsorption. *J Biomater Sci Polym* 18:37–41
80. Misdan N, Ismail AF, Hilal N (2016) Recent advances in the development of (bio) fouling resistant thin fi lm composite membranes for desalination ☆. *DES* 380:105–111
81. Satarkar NS, Biswal D, Hilt JZ (2010) Hydrogel nanocomposites-a review of applications as remote controlled biomaterials.Pdf. *Soft Matter* 6:2364–2371
82. Jing J, Hongkai W, Zhong H, Yang L, Jun Wei JL (2015) IPN hydrogel nanocomposites based on agarose and ZnO with antifouling and bactericidal properties. *Mater Sci Eng C* 61:376–386

83. Krupa AND, Vimala R (2016) Evaluation of tetraethoxysilane (TEOS) sol-gel coatings, modified with green synthesized zinc oxide nanoparticles for combating microfouling. *Mater Sci Eng C* 61:728–735 Evaluation of tetraethoxysilane (TEOS) sol-gel coatings, modified with green synthesized zinc oxide nanoparticles for combating microfouling
84. Meyer A, Baier R, Wood CD, Stein J, Truby K, Holm E, Montemarano J, Kavanagh C, Nedved B, Smith C, Swain G, Wiebe D (2006) Contact angle anomalies indicate that surface-active eluates from silicone coatings inhibit the adhesive mechanisms of fouling organisms. *Biofouling* 22:411–423
85. Selim MS, El-Safty SA, El-Sockary MA et al (2015) Tailored design of Cu₂O nanocube/silicone composites as efficient foul-release coatings. *RSC Adv* 5:19933–19943
86. Jiang S, Sreethawong T, Lee SSC et al (2015) Fabrication of copper nanowire films and their incorporation into polymer matrices for antibacterial and marine antifouling applications. *Adv Mater Interfaces* 2:1–8
87. Arukalam IO, Oguzie EE, Li Y (2016) Journal of colloid and Interface science fabrication of FDS-modified PDMS-ZnO nanocomposite hydrophobic coating with anti-fouling capability for corrosion protection of Q235 steel. *J Colloid Interface Sci* 484: 220–228
88. Eduok U, Faye O, Szpunar J (2017) Recent developments and applications of protective silicone coatings: a review of PDMS functional materials. *Prog Org Coatings* 111:124–163
89. Sankar GG, Sathya S, Murthy PS et al (2015) Polydimethyl siloxane nanocomposites: their antifouling efficiency in vitro and in marine conditions. *Int Biodeterior Biodegradation* 104:307–314
90. Selim MS, Yang H, Wang FQ, Fatthallah NA, Yong Huang SK (2018) Silicone/ZnO nanorod composite coating as a marine antifouling surface. *Appl Surf Sci* 446:40–50
91. Zhang J, Huang W, Han Y (2006) Wettability of zinc oxide surfaces with controllable structures. *Langmuir* 22:2946–2950
92. Bharathidasan T, Dhandapani P (2015) Zinc oxide-containing porous boron-carbon-nitrogen sheets from glycine-nitrate combustion: Synthesis, self-cleaning and sunlight driven photocatalytic activity. *Appl Mater Interfaces* 7:18450–18459 Zinc Oxide-Containing Porous Boron-Carbon-Nitrogen Sheets from Glycine-Nitrate Combustion: Synthesis, Self-Cleaning, and Sunlight-Driven Photocatalytic Activity
93. Lejars M, Margailan A, Bressy C (2012) Fouling release coatings: a nontoxic alternative to biocidal antifouling coatings. *Chem Rev* 112:4347–4390
94. Nurioglu AG, Esteves ACC, de With G (2015) Non-toxic, non-biocide-release antifouling coatings based on molecular structure design for marine applications. *J Mater Chem B* 3:6547–6570
95. Kyrikou I, Briassoulis D (2007) Biodegradation of agricultural plastic films: a critical review. *J Polym Environ* 15:125–150
96. Gross RA, Kalra B (2002) Biodegradable polymers for the Environment. *Science* (80-) 297:803–807
97. Xie Q, Xie Q, Pan J, Ma C, Zhang G (2018) Biodegradable polymer with hydrolysis-induced zwitterions for Antibiofouling. *Appl Mater Interfaces* 10:11213–11220
98. Shaik MR, Korsapati M, Panati D (2012) Polymers in controlled drug delivery systems. *Int J Pharma Sci* 2:112–116
99. Á PG, Mayadunne R, Adhikari R (2006) Recent developments in biodegradable synthetic polymers. *Biotechnol Annu Rev* 12:301–347
100. Vainionp S, Rokkanen P (1989) Surgical applications of biodegradable polymers in human tissues. *Prog Polym Sci* 14:679–716
101. Kolybaba M, Tabil LG, Panigrahi S et al (2003) Biodegradable Polymers: Past, Present, and Future. *Am Soc Agric Biol Eng* 0300:1–15
102. Dai G, Xie Q, Ma C, Zhang G (2019) Biodegradable poly(ester-co-acrylate) with Antifoulant pendant groups for marine anti-biofouling. *ACS Appl Mater Interfaces* 11:11947–11953
103. Peng Q, Zhou X, Wang Z, Xie Q, Ma C, Zhang G, Gong X (2019) Three-dimensional bacterial motions near a surface investigated by digital holographic microscopy: effect of surface stiffness. *Langmuir* 35:12257–12263
104. Qi M, Song Q, Zhao J, Ma C, Zhang G, Gong X (2017) Three-dimensional bacterial behavior near dynamic surfaces formed by degradable polymers. *Langmuir* 33:13098–13104. <https://doi.org/10.1021/acs.langmuir.7b02806>
105. Ma J, Ma C, Zhang G (2015) Degradable polymer with protein resistance in a marine environment. *Langmuir* 31:6471–6478. <https://doi.org/10.1021/acs.langmuir.5b01720>
106. Zhang L, Xiong C, Deng X (1995) Biodegradable polyester blends for biomedical application. *J Appl Polym Sci* 56:103–112
107. Ma Z, Hong Y, Nelson DM, Pichamuthu JE, Leeson CE, Wagner WR (2011) Biodegradable polyurethane ureas with variable polyester or polycarbonate soft segments: effects of crystallinity, molecular weight, and composition on mechanical properties. *Biomacromolecules* 12:3265–3274
108. Chen S, Ma C, Zhang G (2017) Biodegradable polymer as controlled release system of organic antifoulant to prevent marine biofouling. *Prog Org Coatings* 104:58–63
109. Yi J, Huang C, Zhuang H et al (2015) Progress in organic coatings degradable polyurethane based on star-shaped polyester polyols (trimethylolpropane and ϵ -caprolactone) for marine antifouling. *Prog Org Coatings* 87:161–170
110. Ma C, Xu L, Xu W, Zhang G (2013) Degradable polyurethane for marine anti-biofouling. *J Mater Chem B* 1:3099–3106
111. Xu W, Gan T, Zhang G (2014) Marine biofouling resistance of polyurethane with biodegradation and Hydrolyzation. *ACS Appl Mater Interfaces* 6:4017–4020
112. Ma J, Ma C, Yang Y et al (2014) Biodegradable polyurethane carrying Antifoulants for inhibition of marine biofouling. *Ind Eng Chem Res* 53:12753–12759
113. Yang J, Li L, Ma C, Ye X (2016) Degradable polyurethane with poly(2-ethyl-2-oxazoline) brushes for protein resistance. *RSC Adv* 6:69930–69938
114. Ou B, Chen M, Huang R, Zhou H (2016) Preparation and application of novel biodegradable polyurethane copolymer. *RSC Adv* 6:47138–47144. <https://doi.org/10.1039/C6RA03064E>
115. Yao J, Chen S, Ma C, Zhang G (2014) Marine anti-biofouling system with poly(ϵ -caprolactone)/clay composite as carrier of organic antifoulant. *J Mater Chem B* 2:5100–5106
116. Chen S, Ma C, Zhang G (2016) Biodegradable polymers for marine antibiofouling: poly(ϵ -caprolactone)/poly(butylene succinate) blend as controlled release system of organic antifoulant. *Polymer (Guildf)* 90:215–221
117. Fay F, Linossier I, Valle K (2007) Biodegradable poly(ester-anhydride) for new antifouling coating. *Macromolecules* 8:1751–1758
118. Fay F, Linossier I, Langlois V, Renard E, Vallée-Réhel K (2006) Degradation and controlled release behavior ϵ -caprolactone copolymers in biodegradable antifouling coatings. *Biomacromolecules* 7:851–857
119. Fay F, Linossier I, Renard E, Valle K (2007) Poly(ϵ -caprolactone-co-d-valerolactone) as new degradable binder used for antifouling paint. *Eur Polym J* 43:4800–4813
120. Loriot M, Linossier I, Vallée-Réhel K, Fay F (2017) Influence of biodegradable polymer properties on antifouling paints activity. *Polymers (Basel)* 9:36
121. Azemar F, Fay F, Réhel K, Linossier I (2015) Development of hybrid antifouling paints. *Prog Org Coatings* 87:10–19
122. Zhou X, Xie Q, Ma C et al (2015) Inhibition of marine biofouling by use of degradable and Hydrolyzable Silyl acrylate copolymer. *Ind Eng Chem Res* 54:9559–9565

123. Xie Q, Ma C, Zhang G, Bressy C (2018) Poly(ester)–poly(silyl methacrylate) copolymers: synthesis and hydrolytic degradation kinetics. *Polym Chem* 9:1448–1454
124. Dai G, Xie Q, Chen S et al (2018) Biodegradable poly (ester) - poly (methyl methacrylate) copolymer for marine. *Prog Org Coatings* 124:55–60

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