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Adhesion of Fouling Organisms and its Prevention Technique

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Abstract - Biofouling is the undesirable accumulation of microorganisms, plants, algae and animals on submerged structures especially ship hulls. Biofouling also occurs on the surface of living marine organisms. It is also found on membrane systems such as membrane bioreactors and reverse osmosis spiral wound membranes.The application of TBT and other heavy metal-based antifoulants has created another environmental problem.This review article summarizes the adhesion mechanisms of biofouling organism, type of biofuels and technique to prevent artificial surfaces from marine fouling organisms. The antifouling methods based on traditional chemical methods, biological methods, and physical methods are discussed. The chemical methods include such as tributyltin self-polishing copolymer base coatings, it has good performance among the other coating but this coatings cause's serious environmental problem. Hence, we focus on other antifouling coatings include coatings with a base on copper acrylate, TBT free self-polishing copolymer coating, Non-toxic antifouling Coating mostly silicon base chemistry, Biological antifouling methods including Enzymes that degrade adhesive used for settlement, Enzyme that disrupt the biofilm matrix, Enzyme that generates deterrents and biocides, Physical methods. In this review paper, most of the focused-toxic antifouling technologies are discussed. It is concluded that Low Surface Energy Anti-fouling Coatings, Modified Organic Silicone Anti-fouling Coatings, Modified Organic Fluorine Anti-fouling Coatings, Fluorine Silicone Resin Anti-fouling Coatings because of their excellent effectiveness and low toxicity.

Biofilm, Microorganism, Macroorganism, Adhesion Mechanism, Antifouling Methods.

INTRODUCTION

Marine biofouling is a global problem that is detrimental to both moving ships and static underwater devices. Marine microorganisms tend to attach to any unprotected surface and grow into biofilm, which can be hardly removed even under high shear flow condition [1]. With the long-term accumulation of marine organisms, ships suffer significantly from the increase on the net weight as well as the drag when cruising.Increased drag causes fuel power penalties of up to
86% at cruising speed, it is notable even a very thin layer of diatom slime would result in 10%–16% penalty [2]. Billions of dollars have been spent globally each year to remove biofouling on ship hulls and marine devices [1]. In addition, increased fuel consumption brings up concerns on the emission of greenhouse gas. Therefore, preventing the biofouling beneficial in both economic and environmental aspects.

Fuel consumption increases of about 40% have been observed because of biofouling and the cost of a one-way has increased by about 77% due to ship's hull fouling[3] more expensive and time consuming, hull maintenance, because dry-docking operations need to be more time. Cleaning processes generate a large number of toxic substances that are discharged into the ocean.

In the marine industry, biofouling is a huge problem, and research is focused on the development of an effective anti-fouling solution. However, the mechanism of biological adhesion needs to be determined to allow development of antifouling paint. In this review, we have discus adhesion mechanism of fouling organism on an artificial surface and deferent types of antifouling method to remove the biomass or fouling organism.

1. BIOFOULING

Marine biofouling can be defined as the undesirable adhesion to surfaces and further growth of organisms. Mainly biofilm-forming microbes, macro-algae, and invertebrates that are defined as foulers or biofuels [3]. (Fig.1)The adsorption of a conditioning film of macromolecules, primary colonizers, consisting of microorganisms such as bacteria, microalgae or other pioneer microorganisms, are found on surfaces after only a few minutes to hours of immersion. Secondary colonizers, consisting mostly of protozoa and spores of macroalgae, settle and start to grow on unprotected surfaces within a week. Lastly, larvae of hard macrofoulers (or tertiary colonizers, e.g. barnacles, mussels, tubeworms, bryozoans) will settle on unprotected surfaces 2-3 weeks after immersion [3].

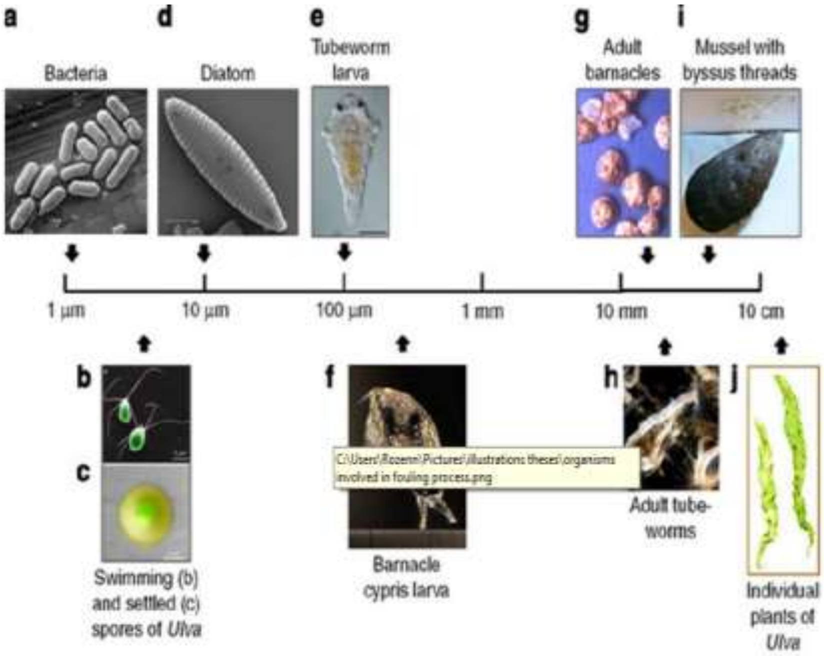


Figure 1: Organisms involved in the fouling process [2].

1.1 Biofouling organisms and their adhesion mechanism.

More than 4000 marine fouling species have been observed globally, most of which live primarily in the shallower water along the coast and in harbors that provide abundant nutrients [4]. The severity of biofouling depends on a large number of parameters, including water hardness, temperature, salinity, light, location, season, depth, and in case of ship travel speed [4]. In general, marine adhesion organisms can be divided into two major categories. The first of these includes the micro-fouling or biofilm organisms, which are bacteria and diatoms [4]. Biofilms are omnipresent, as long as the surfaces are exposed to water. The other category includes macro-fouling organisms such as algae and barnacles. The most important macrofouling species are barnacles' mussels, Polychaeta worms, bryozoans, mussels, bryozoans and seaweed [7].

Figure 2-Ship hull with Seaweed

The biofilm develops as bacteria and microalgae adhere to the surface. Microorganism colonization involves two distinct steps: reversible adsorption, and irreversible adhesion. The former is governed mainly by physical effects such as Brownian motion, electrostatic interaction, gravity, water flow and van der Waals forces [80].The latter occurs mainly through biochemical effects such as secretion of extracellular polymeric substances (EPS). During biofilm formation in the marine environment, diatoms are the most important contributors. It has been reported that microfouling alone can increase fuel consumption by up to 18%, and reduce the sailing speed by at least 20% [11].

After the formation and development of the biofilm, larvae or spores of macrofoulers will attach to the surface. Two or three weeks later, these will finally evolve into a complex biological community [18]. In marine immersion experiments, adhesion of microorganisms usually occurs after biofilm formation. However, this is not always the case, for instance, the larvae of some species of bryozoans polychaetes and some other biofoulers adhere before biofilm formation.

Therefore, the process of biofouling occurs by both physical reactions and biochemical reactions. The physical reactions are governed by factors such as electrostatic interaction and water flow and lead to the formation of the conditioning biofilm and adsorption of microorganisms [18]. The biochemical reactions include EPS secretion, movement and secondary adhesion of microorganisms, the formation of the biofilm, and adhesion of macrofoulers. Whereas the physical reactions are usually reversible, the biochemical reactions are effectively irreversible. Thus, it would be easier to prevent biofouling during the physical reactions rather than the biochemical reactions. Successful inhibition of the physical reactions would constrain the later biochemical reactions. The biofouling mainly divided into three category such bacteria, microalgae and microorganisms [6].

1.2 Bacterial adhesion

The process of bacterial attachment to an available surface and the subsequent development of a biofilm can be described in simple or incredibly elaborate. The process is dictated by a number of variables, including the species of bacteria, surface composition, environmental factors, and essential gene products. As an oversimplified rule of thumb, primary adhesion between bacteria and abiotic surfaces is generally mediated by nonspecific (e.g., hydrophobic) interactions [17].

Bacterial adhesion occurs due to the interaction of planktonic cells with the surface by physical reactions, such as electrostatic interactions, gravity, and water flow [25]. Initially, reversible absorption takes place, then bacteria uses extracellular polymers to temporarily adhere to the surface. These polymers are mainly glucose and fructose-based polysaccharide fibrils [81]. The biofilm is formed when the bacterial communities secrete more EPS.

Microorganisms are commonly perceived to be free-floating and solitary (i.e. planktonic). However, under natural conditions, most microorganisms tend to attach to surfaces and eventually form biofilms [18]. The initial attachment is reversible. As the bacteria multiply, they become more firmly attached and differentiate, changing gene expression patterns in ways that promote survival Once firmly attached, the bacteria begin to secrete a surrounding matrix known as extracellular polymeric substance (EPS). This is a protective matrix or ‘slime’. Small bacterial colonies then form an initial biofilm (Figure 3) [18].

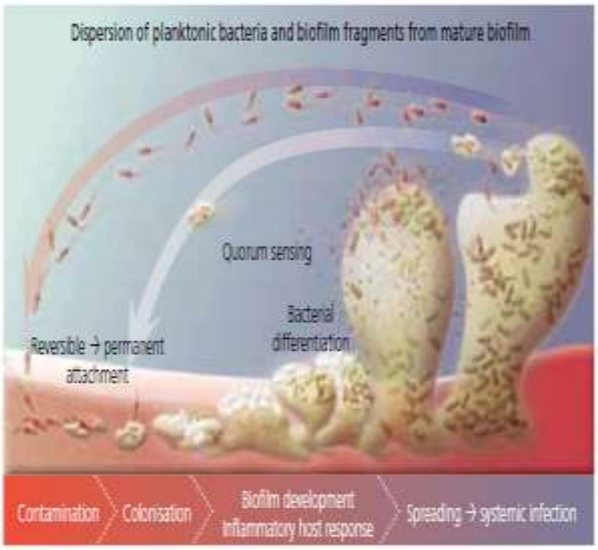


Figure 3.Biofilm formation in four steps: initial adsorption, irreversible adhesion, permanent surface attachment, slimy protective matrix/biofilm maturation and dispersion (Phillips PL, Wolcott RD, Fletcher J, Schultz GS [18]

1.3 Microalgae adhesion

In the marine environment, eukaryotic fouling microorganisms are diatoms, fungi, and protozoan, and the dominant organisms are diatoms.Diatom adhesion is a complex process, as most of the diatoms lack flagella, they cannot actively approach a given surface but rather passively land on the substratum. Benthic diatoms approach surfaces through the effects of either gravity or water flow [72]. Plankton diatoms, which have almost the same specific gravity as seawater, land on surfaces mainly through turbulence [14]. The electrostatic interactions such as Coulomb attraction and electrostatic contact potential are also involved. During contact between diatoms and a surface, van der Waals forces may also operate and this has been observed in other adhesive situations [3].

Initially the diatoms land on the surface, they actively form the initial reversible attachment called reversible surface attachment primary adhesion through secretion of EPS. The diatoms move along the surface of the artificial structure to get better positions for attachment called as diatom gliding.

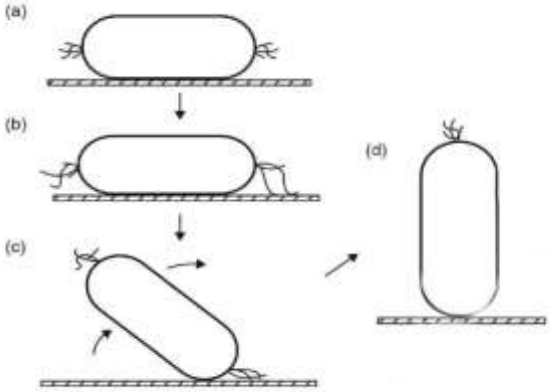


Figure 4: Diagram showing the initial adhesion process of the diatom Stauroneisdecipiens [8](a): landing on the girdle or the side, (b): contact and interactions between the motility and the adhesion complex, (c) and (d): pull of the cell onto the raphe.

EPS of diatoms is made by carboxylate or sulphated acidic polysaccharides, which are involved in the reversible adhesion, and proteoglycans, which are involved in diatom gliding and cross-linking stabilization of the biofilm matrix [8] The composition of EPS produced by different types of diatoms are diverse [77] and include various protein fractions and complex anionic polysaccharides with heterogeneous combinations of monosaccharide [78]. In addition, at least two types of mucilage can be detected for the same species of diatom [79]. After the adhesion, the microorganisms begin to multiply while sending out chemical signals that intercommunicate among the bacterial cells [19].

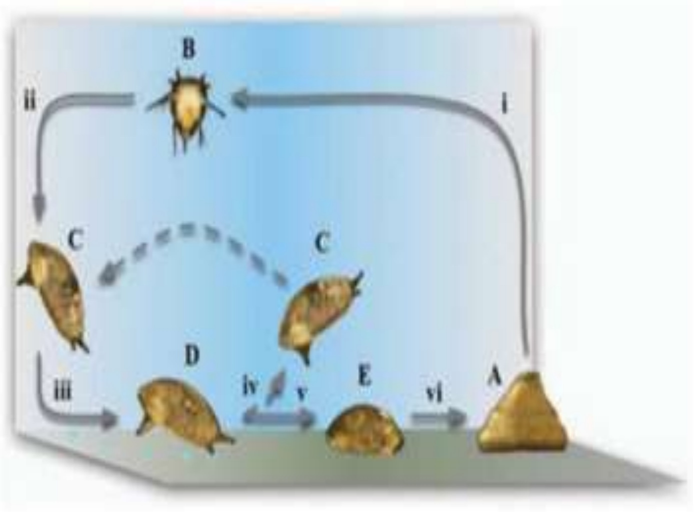
After the adhesion, the microorganisms begin to multiply while sending out chemical signals that intercommunicate among the bacterial cells. The cells multiply within the embedded exopolysaccharide matrix, thus giving rise to the formation of micro-colonies and this micro-colonies spread over the surface to form a big mass of microalgae.

On the basis of review articles, The diatoms attached to surface initially than after maturation pried it spread over the surface to form biomass.

1.4 Macroorganism adhesion

The common problematic biofouling effects arise due to the colonization of microorganisms such as spores of macroalgae, barnacle larvae, bryozoans, mollusks, polychaete, tunicates, and coelenterates [14].

Especially hard foulers, such as barnacles and mussels, have a major impact on the hydrodynamic properties of ship hulls, namely increased hydrodynamic drag and thus increased fuel consumption [21. 22]. As for the zoospores of algae, antifouling tests targeting barnacles frequently focus on the sessile stage, which are cyprids that hatched from the adult organisms [20]. The two conventional approaches to study the interaction of these microorganisms with a surface involve settlement assays of competent larvae [23] and/or the mechanical removal of adult's organisms in order to estimate the adhesion strength [20]. A simplified life-cycle of barnacle starts with nauplii (B) released by adult barnacles (A) [23]. After some time of feeding (from days to months), then metamorphose into cyprids (C). These cyprids explore surfaces (D) and sometimes deposit footprints during exploration. If the surface is not satisfactory, they leave into the water column (C), otherwise, they settle permanently (E). Within 12 h of permanent attachment, they complete the metamorphosis into a juvenile barnacle (A). Hence, phase D is the stage when cyprids actively probe the surface.



The fig.5 simplified life cycle for a generalized thoracic and barnacle, illustrating site selection and settlement by cyprids followed by metamorphosis. Letters (A–E) indicate stages in the development of barnacle and numerals (i–vi) indicate behaviors. A is a juvenile barnacle. Within a few months, this barnacle will be sexually mature and able to release nauplii, (B) into the water column from eggs brooded within the mantle cavity. After feeding in the water column for days to weeks (i–ii) the nauplii metamorphose into cyprids (C). When competent, the cyprids migrate to the benthos (iii) and explore surfaces, depositing footprints as they explore (D). Cyprids may reenter the water column if the surface is not satisfactory, thus delaying settlement (iv), or settle immediately (v) if stimulated to do so. (E) Permanently attached (settled) cyprids. Within 12 h of permanent attachment, cyprids will complete metamorphosis (vi) into a juvenile barnacle (A) [23].

Figure 6-Ship hull with barnacles

The increased diatom concentrations could induce maturation of barnacle larva. This has been demonstrated in a variety of marine organisms such as barnacles, oysters, and Ulva fed by bacteria and diatoms. Because of competition for nutrients and light, it is believed that microorganisms produce metabolites to repel specific microorganisms.

The surface cues responsible to induce settlement and adhesion of barnacle. A systematic understanding is complicated by the fact that different barnacle species show different responses. To observe settlement behavior, tracking techniques are well suited as they allow visualizing how the exploration process and the sensing of the surface are influenced by the surface properties. The probability that barnacles initiate the adhesion process and metamorphose into a juvenile barnacle depends on the properties of the surface. The influence of surface energy and surface charge due to the settlement of barnacle’s [24]

2 ANTIFOULING METHODS

Within the marine environment, any surface in contact with seawater suffers from bio-fouling by marine organisms. When these organisms, such as algae and barnacles, attach to the hull of a ship performance of the vessel is compromised. Fouling on hulls increases fuel costs significantly, creates extra wear on engine components due to extra power to move ships and can ultimately cause engine failure if water intakes for cooling become blocked. Increased maintenance costs also occur as a result of fouling as ships need to be dry docked more frequently for cleaning.

There are many factor influence biofouling organisms including temperature, salinity, light, geography, depth, and voyage speed [4]. Biofouling is generally grown rapidly in high water temperature because of breeding periods and rates of growth with a temperature of water for biofouling organisms. Therefore, to effectively prevent biofouling, many type coatings have been investigated to chemically inhibit the fouling organisms [3]. Influence of microscale physical factors on biofouling has been researched and some new antifouling technologies have developed that involve changing physical factors. The microorganisms can secrete metabolites that inhibit the attachment of some microorganisms, and concentrated extracts of these metabolites could also be effective antifouling agents [4].

In short antifouling methods can be divided into three class: chemical, physical, and biological methods in which today's date chemical method most effective rather than physical and biological methods.

2.1 Traditional chemical methods

Many types of antifouling methods have been investigated over this time [4]. A variety of paints was developed the mid-1800s based on the idea of dispersing a toxicant in a polymeric vehicle. Copper oxide, arsenic, and mercury oxide were popular antifoulants. Solvents included turpentine oil, naphtha, and benzene. Linseed oil, shellac varnish, tar, and various kinds of resin were used as binders [28]. In 1841, Mallet patented an antifouling paint in which slightly soluble coatings of poisonous materials were applied over a coat of varnish. This invention did not work because of abrasion and lack of control of the solution rate [28]. In 1847, William John Hay applied the studies by Sir Humphrey Davy and invented a successful coating based on the idea of isolating the iron hull from a coating containing copper compound powder by means of a non-conductive varnish [29]. In 1860, James McInness used copper sulphate as antifoulants in a metallic soap composition. This ‘hot-plastic paint’ was very similar to ‘Italian Moravian’ paint, the best at the time, which was a mixture of rosin and copper compound developed at the same time in Italy [28]. In 1863, James Tarr and Augustus Wonson were granted a US patent for A/F paint using copper oxide in tar with naphtha or benzene [28]. At the end of the 19th century, ‘Italian Moravian’ and McInness ’‘hot-plastic paints’, shellac type paints (rust preventive), and various copper paints were widely used. These paints were applied over a first coat of anticorrosive shellac or varnish, or of the same composition as the antifouling coating but without containing the toxicant [28]. These paints were expensive, relatively ineffective and their lifespan short [28].

Since the late 20th century, organic tin and its derivatives have been widely used as antifouling coatings because of their activity against a wide range of fouling species. Organotin compounds that have been used as antifoulants include tributyltin oxide and tributyltin fluoride.

In insoluble matrix paints (also termed contact leaching or continuous contact [14], the polymer matrix is insoluble and does not polish or erode after immersion in water. A variety of commercial high molecular weight polymers can be used, and typical examples are insoluble vinyl, epoxy, acrylic or chlorinated rubber polymers [30]. The species dissolved by the sea water penetrating into the film have to diffuse through the interconnecting pores formed after the dissolution of the soluble pigments. After a certain time in service, the dissolved pigment ions have to diffuse through such a thick leached layer that the rate of release falls under the minimum value required to prevent fouling [31] as shown in Fig. 7. These types of structures are mechanically strong, not susceptible to cracking and generally resistant to atmospheric exposure in non-aqueous environments (stable to oxidation and photodegradation [31]. The short (12–18 months [30] lifetimes of these products have limited the number of vessels applying this kind of paints.

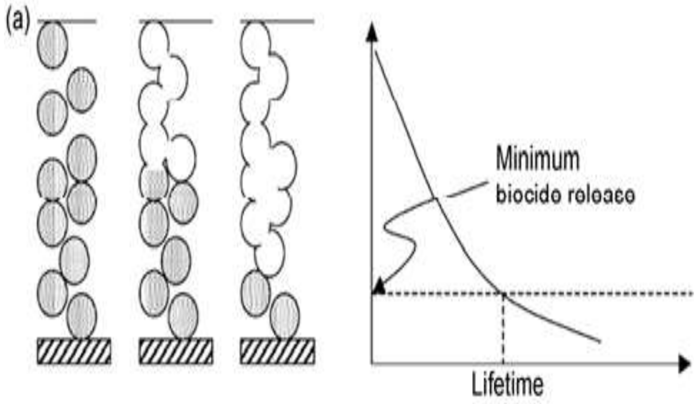


Figure 7: Method of release and biocide release rates of insoluble matrix paints [31].

Soluble matrix paints were developed in order to avoid the loss of A/F efficiency with time by incorporating a binder which could be dissolved in seawater. The classical film-forming material in these systems contains high proportions of rosin. Rosin is a natural and very compatible resin obtained from the exudation of pine and fir trees [32].Its variable composition, which contributes to a rather unpredictable performance of natural rosin-based paints, consists generally of about 85–90% of acidic materials (resin acids), of which the abiotic (C30) and levopimaric (C30) acids are the most important [32]. Each of these acids contains two double bonds and a carboxyl group. These conjugated double bonds affect the stability of the resin and make it oxidable when exposed to air. This undesirable feature had to be taken into account during dry-docking, as the application of the paint could only be performed a short time before immersion. Once in contact with sea water, the carboxyl groups reacted with sodium and potassium ions present in the sea water, and thus gave resonates of high solubility. The resulting high dissolution rate in seawater and the brittleness of rosin forced its blending with plasticizers and co-binders [32]. These ingredients provided the binder system with the required film-forming and mechanical properties together with a suitable dissolution rate. Nevertheless, in static conditions, these compounds, and sometimes soaps formed with calcium and magnesium [32], were not easily released into the bulk phase.

The lifespan of antifouling coatings, soluble matrix antifouling coatings were developed. As implied by the name, both the toxic materials and matrix, which contains a great amount of resin, can dissolve in seawater [4]. In this case, the leached layer can be much thinner and toxic materials deeper in the film can be easily exposed to water, which lengthens the lifespan of the antifouling coating.

The still deficient performance of both insoluble and soluble matrix technology encouraged the development of many other alternatives different from biocide-based coatings. The study of such systems was partially abandoned after the development of TBT-based paints and has been resumed after the first regulations against them. Among all the different ideas proposed, the use of electrical current is the most common and has been studied from the end of the 19th century [33].

2.2 Modern chemical antifouling methods

There are major three types modern chemical technologies used to prevention from fouling organism as tributyltin self-polishing copolymer coatings, tin-free SPC coating, and non-toxic antifouling coating.

2.2 Tributyltin self-polishing copolymer coatings.

Montermoso and co-workers have first suggested the possibilities of TBT acrylate esters as antifouling coatings in 1958 [34]. Six years later [37], James patented the use of organotin copolymers including copolymers of TBT acrylate and methyl methacrylate. TBT self-polishing copolymer (TBT-SPC) technology, patented by Milne and Hails in1974 [38], revolutionized the antifouling paints and the shipping industries. Originally, ZnO was used as a pigment together with insoluble pigments [36]. The poor antifouling activity of zinc ions was compensated for by high polishing rates. The shift to cuprous oxide made it possible to reduce the polishing rates and attain a better efficiency against algal fouling [36].

In 1985, the hydrophobicity of the monomers as a means of controlling the polishing rate was introduced. All these advances led to the most successful antifouling system ever. An analysis of the reasons that made it such a good system may show the way towards an equally efficient substitute.Tributyltin self-polishing antifouling paints are based on an acrylic polymer (usually methyl methacrylate) with TBT groups bonded to the polymer backbone by an ester linkage [35]. After immersion, the soluble pigment particles in contact with seawater began to dissolve. The copolymer of TBT methacrylate and methyl methacrylate in the paint is hydrophobic, which prevents seawater from penetrating the paint film [35]. Thus, seawater can only fill the pores created by the dissolution of the soluble pigment particles. The carboxyl–TBT linkages hydrolytically unstable under slightly alkaline conditions [37]. This is usually the case of marine waters, and results in a slow, controlled hydrolysis that cleaves the TBT moiety from the copolymer. This hydrolysis reaction takes place, to a varying extent, throughout the leached layer [39]

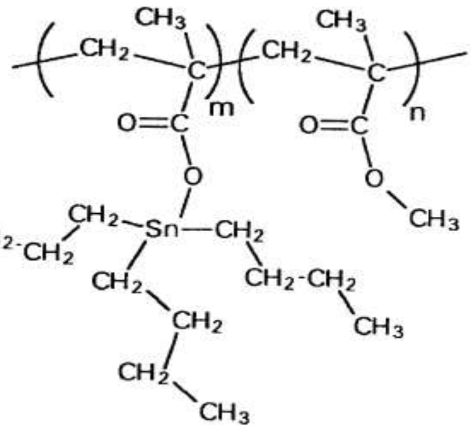


Fig. 8. The chemical formula of a repeating unit of a copolymer of tributyltin methacrylate (TBTM) and methyl methacrylate (MMA) [39], with permission of American Chemical Society).

Typical commercial TBT-SPC paints are formulated to have a polishing rate in the broad range of 5–20 m per month [35]. The main advantage of these systems is that it has been possible to manipulate the polymer chemistry so as to customize the rate of reaction (and thus "polishing" and biocide release rates) of the polymer in order to give maximum effective lifetime [35]. In addition, the composition of the binder can be tailor-made through carefully controlled polymerization conditions. This has allowed the paint industry to design different antifouling paints for ships with different activities High-speed vessels use slow polishing products, while slow vessels with long stationary periods apply fast polishing coating maintaining sufficient biocide release rates for fouling control. Consequently, practically all vessels can delay dry-docking periods up to 5 years [40].

As mentioned in above data, both soluble and insoluble matrix antifouling coatings have their deficiencies. Consequently, alternative coatings have been investigated. In 1974 [4].

TBT-SPC paints having good mechanical strength, good stability to oxidation, and short drying times. The unavoidable formation of biofilm does not largely affect the net biocide leaching and binder reaction rates. During the 1960s the chemicals industry developed efficacious and cost-effective anti-fouling paints using metallic compounds, in particular, the organotin compound tributyltin (TBT). By the 1970s, most seagoing vessels had TBT painted on their hulls

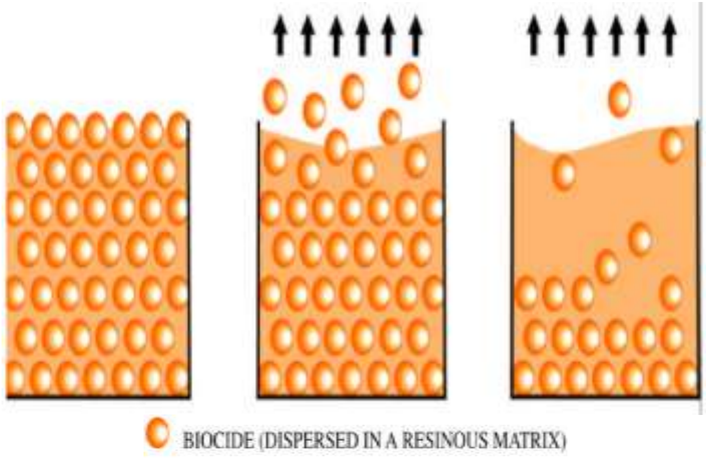


Fig. 9aBiocide leaches freely from the resinous matrix. The initial release is rapid, subsequent release declines so antifouling performance of paint diminishes over time. Source: European Chemical Industry Council (CEFIC).

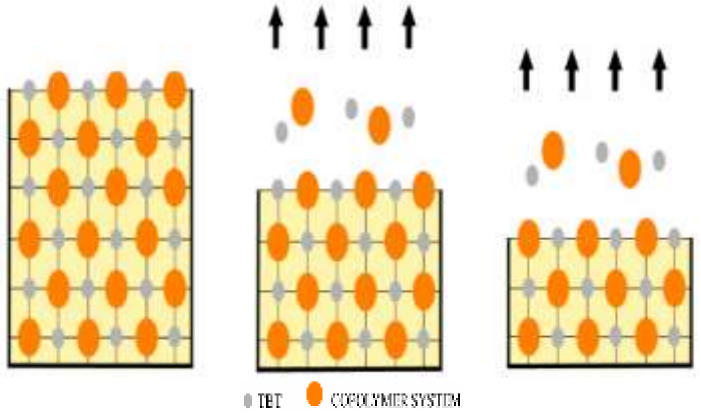


Fig.9 bSea water hydrolyses the TBT copolymer bond and the TBT biocide and copolymer resin is slowly released at a controlled rate. Uniform anti-fouling performance is achieved throughout the lifetime of the paint. Source: CEFIC

TBT base coating having a harmful effect on marine life. The major effect on Water and sediments, shell malformations, Imposex, Marine mammals, reduced resistance to infection.

2.2.2 Tin-free SPC Coating.

The main developments in TBT-free SPC antifouling have been pioneered by Japanese paint companies, in response to the TBT application ban which was introduced in Japan in the early 1990s [41]. A series of new acrylic polymers have been synthesized which attempt to mimic the chemistry of TBT in seawater. There are three main types:

- Copper Acrylate
- Silyl Acrylate.
- Zinc Acrylate.

The first of these to be introduced was the copper acrylate system, launched in 1990 [41]. The copper acrylate polymer reacts with seawater in exactly the same way as the TBT SPC co-polymer, producing a soluble micro-layer at the paint surface, resulting in the gradual “polishing away” of the coating. This mechanism ensures that there is no leached layer build up over time and that the biocides in the system are released in a controlled way, to give long-term fouling protection and with lifetime proportional to the thickness applied.The biocides in the SPC products are a copper oxide and zinc pyrithione. Copper [43] itself is safe to man and the environment when used in antifouling paints for ships,

Zinc pyrithione is degraded and becomes-toxic quickly after release from the coating. The other major use of zinc pyrithione is an antidandruff agent in shampoos.

In copper-based antifouling coatings, copper is added as copper metal, oxide (Cu_2O), thiocyanates (CuSCN) or sulfides (Cu_2S), resulting in different colored paints. Cu_2O, the most widely used, is a red pigment, Cu_2S is black and CuSCN is white [44]. Although the use of copper in antifouling products in aquaculture poses its own environmental problems, it is far less toxic than TBT, and, since the ban on organotin antifouling formulations, copper-based antifoulants have experienced are renaissance [45].

The tin-free anti fouling coatings can be divided into two categories: controlled depletion systems (CDPs), and tin-free self-polishing copolymers (tin-free SPCs). Their AF efficacy lasts between 12 months (contact leaching coatings) and up to 90 months for the most efficient SPCs. These chemically active AF paints typically contain 35-50 wt.% of dicopper oxide as the main biocide, and less than 10 wt.% of co-biocides or booster biocides such as copper pyrithione, zineb, and DCOIT (4,5-dichloro-2-octyl-2H-isothiazol-3-one). The former coatings upgrade the traditional soluble matrix technology by incorporating modern reinforcing resins with the same AF mechanism as the conventional resin matrix paints. The latter coatings function in a similar manner to TBT-SPC but do not contain tin. Beside Zinc, the majority of tin-free AF paints currently available contain copper, and some contain silver [46]. Currently, the major copper compounds used for AF include metallic copper, cuprous thiocyanate and cuprous oxide [47] Copper ions as Cu^{2+} have a major role in antifouling paint.

Copper toxicity from AF sources becomes a problem in the marine environment, especially in isolated water bodies such as enclosed marinas and harbors that experience little water exchange combined with high levels of boating activity [48].

2.2.3 Non-toxic antifouling Coating.

A. Low Surface Energy Anti-fouling Coatings

Low surface-energy anti-fouling paint has very low surface energy, making it difficult for marine fouling organisms to attach to the hull. Such anti-fouling paint is divided into two types including silicone-based and contains fluoride [49]. In 1972, American researcher first developed silicone-based anti-fouling paint successfully and got the patent. The anti-fouling valid of this material was up to 2-3years. Although the surface energy of silicone is low, its adhesion is weak. So it is necessary to improve the enhancing adhesion of the silicone. Fluorocarbon resin has strong weather resistance, water and oil resistance, stain resistance, chemical resistance, solvent resistance etc. thus it is a kind of excellent material for super weather-resistant, anticorrosive and architectural paint [50]. Organic fluoropolymer was applied in the US military at first and Polytrifluorochloroethylene (PCTFE) in the 1860s. Afterwards, Fluorine paint has exhibited superior performance in the low surface energy anti-fouling paint, and it obtained widespread concern.

B. Modified Organic Silicone Anti-fouling Coatings.

Silicone resin series polymer has a special skeleton for a unique function for silicon resin polymers, such as low surface energy and low elastic modulus. It is difficult for marine life to attach because of its low surface tension. Silicone resin polymer seeks to be the rich for linear, elastic, fluid skeleton and there is adequate the active side group surface to decrease the surface energy [51]. Silicone could not stop marine biofouling, but it could reduce the adhesive strength. At the same time, exudation of oil could cut down the marine fouling and promote marine life off with the scouring effect of seawater [52]. The polysiloxane with tin through the process of inducing organic tin compounds with strong biological activity to polysiloxane molecules. This method solves the volatility problem of tin compounds and decreases the toxicity of the polymer [53]. Silicone antifouling paint has experienced the development process from silicone rubber to modified silicone resin since the 1960s. Now, researchers mainly use silicone polymer, modified silicone resin, and pigment filler reinforced resin to improve the performance of anti-fouling coatings for low surface energy.

C. Modified Organic Fluorine Anti-fouling Coatings.

The durability and resistance to chemicals of the fluoride-containing polymer are excellent, but the price is expensive.So researchers modify them to get good anti-fouling coatings.Organic fluorine polymer was first developed in the UnitedStates in the 1930s for the needs of the military industry. In 1938, In the United States developed PTFE and the non-adhesive coating was invented. But this paint could not be cured at room temperature and has high sintering temperature. Also, the conventional organic solvent is difficult to dissolve this paint.In 1982.The developmentfluorocarbon coatings [54]. This kind of paint has a high gloss and transparency, soluble in conventional organic solvents, and can be cured at room temperature. The appearance of this kind of fluorocarbon coatings has greatly expanded the application of fluorocarbon coatings.

D. Fluorine Silicone Resin Anti-fouling Coatings

The mechanical property of silicone resin is poor and is not resistant to organic solvents, but the flexibility is good.The fluorine resin has excellent properties, and the side groups can improve the solvent resistance and improve the surface properties, but the price is very expensive. Therefore, researchers have developed a new type of anti-fouling coating which has both advantages.The synthesized resin coating containing silicon and fluorine. The coating is hydrophobic and oleophobic properties and the release rate of Ulva is higher than 80% which showed good anti-fouling effect [54].Chen et al. modified acrylic resin using organic silicon and organic fluorine monomer. The result showed that when the content of silicon monomer is 9%, the surface tension of the coating is higher, which has a better antifouling effect [55].

E. Conductive Anti-fouling Coating

The conductive anti-fouling coating is using conductivity of the system, electrolyze seawater, hypochlorite produced and then prevent the pollution. One method is coat the boat with a layer of a conductive polymer, then the boat is a cathode and the conductive coating is an anode. Through the microcurrent,

ClO_4^- layer formed on the surface of the coat and to achieve the effect of antifouling. Polyanilinecoating, the coating had the special vulnerability and the anti-fouling performance can be maintained for 6~9 months [56].

3. Biological antifouling methods

Some organisms are able to secrete enzymes or metabolites that have low-toxicity and biodegradable to inhibit the growth of their competitors. Many attempts have been made by researchers to extract high concentrations of secondary metabolites for biological antifouling. The functional antifouling components have been reported in organisms such as fungi [57], sponges [58] and some bacteria ([59]. Various enzymes have been reported with antifouling properties such as oxidoreductase, transferases, hydrolase, lyase, isomerase, and ligase [60]. In general, the function of enzymes for antifouling applications can be divided into the following four categories:

3.1 Enzymes that degrade adhesive used for settlement

In macrofouling, protein and proteoglycans have an important role in the adhesion step. Proteases can hydrolyze peptide bonds at different sites. Thus, these enzymes can be used to degrade mucilage based on the peptide to prevent biofouling. One example is the attachment of Ulva spores, barnacle cyprids and bryozoans were effectively inhibited by serine protease [59] [61] by reducing the adhesive effectiveness rather than any toxic effect. However, the process is more complicated in microfouling ([62], because the polysaccharide-based adhesive is as important as proteins during secondary adhesion. In general, glycosylase mediated the polysaccharide degradation and the process is difficult and quite complex [61] Glycosylase can target only limited range or linkages. Therefore, it would be difficult to choose an appropriate glycosylase for broad-spectrum antifouling [62].

3.2 Enzyme that disrupts the biofilm matrix

The varieties of EPS make biofilm very complex substances. Thus, a very broad combination of both hydrolyzes and lyases are required to disintegrate their polymeric network (Jakob et al., 2008). Biofilm is very adaptable to external conditions, the degradation of the crucial component will induce the generation of alternative components that will replace the original and establish a new network to proliferate the organism (Joao et al., 2005). Tests have shown that even though alginase could detach a thin biofilm, it gave no effect on an identical biofilm that was already fully established (Joao et al., 2005). In conclusion, the antifouling method of disrupting the biofilm matrix may not be suitable and effective due to the complexity and adaptability of the biofilm.

3.3 Enzyme that generates deterrents and biocides

Recent antifouling compounds extracted from metabolites secreted by different marine animals or plants should be classified as deterrents rather than toxins [63]. Some of the enzymes that possess such effect include glucose oxidase, hexose oxidase and haloperoxidase [64]. Glucose and hexose oxidase is used to generate hydrogen peroxide to induce oxidative damage in living cells [65]. Haloperoxidase catalyses the formation of hypohalogenic acids usually used in water treatment systems as disinfecting agents. Hypohalogenic acids have similar characteristics as hydrogen peroxide that has a high rate of decomposing into water and oxygen in seawater, this could be further study as potential nontoxic and biodegradable antifouling substances [64].

3.4 Enzyme that interferes with intercellular communication

Quorum sensing plays an important role in biofilm formation. Some Gram-negative bacteria required N-acyl homoserine lactone (AHL) for quorum sensing mechanism. By first eliminating the AHL autoinducers may thus prevent the development of biofouling [83]. AHL acylase able to degrade AHL and biofilm formation is inhibited by the increasing concentration of this enzyme. The settlement of Ulva spores and polychaete larvae was also affected by acylase to some extent [66].

3.5 Challenges for enzymatic antifouling methods.

The temperature ranges of seawater from - 2°C to 30°Ccan affect the enzyme activity and stability. It is very challenging to balance the effectiveness of the enzymatic antifouling coating and it lifespan because if the temperature is too high, the enzyme will decompose thus decrease the lifespan of the enzymatic antifouling coating. Apart from that, another crucial step in this antifouling method is to design an appropriate coating matrix that contains the enzyme for successful application [82]. More study should be made to analyze the distribution of the enzyme and its amount because soluble enzymes will soon form a thick leaching layer.

4. PHYSICAL ANTIFOULING METHODS

4.1 Antifouling by electrolysis and radiation.

The most common physical method in preventing biofouling is to produce hypochlorous acid (HCIO), ozone bubbles, hydrogen peroxide or bromine through electrolysis of seawater [4]. Their strong oxidizing ability will spread all over the ship's hull and eliminate possible surface for fouling organism's attachment. Some of the systems are not highly efficient due to the large voltage drop across the surface that causes the corrosion problems of steel. Currently, the titanium-supported anodic coating has been suggested with advantages such as having low decomposition tension, higher current efficiency, and lower energy consumption [67] Another method is by microcosmic electrochemical methods that use direct electron transfer between the electrode and the microbial cells. This cause's electrochemical oxidation of the intercellular substances, however, it is expensive and the efficiency has not been established. Vibration method such as acoustic technology has also been reported [68] Hydroids, barnacles and mussels can be inhibited to some extent by either external vibration sources or piezoelectric coating [69] However, this method requires huge power consumption. Other studies have evaluated magnetic fields, ultraviolet radiation and radioactive coatings [4], but these methods are not practical in application. Another potential method is to use substrates with a different color, which affect the attachment and growth of spores and worms [70].

4.2 Antifouling by modification of surface topography and hydrophobic properties

In recent years, varying surface characteristics, including surface roughness, topography, hydrophobic behavior, and lubricity, have been investigated for the antifouling application. Studies had shown that fouling diatoms adhere more strongly to a hydrophobic polydimethylsiloxane (PDMSE) surface than to glass. Bacteria and Ulva spores adhere strongly to the surface with the greater angle and hydrophilic surface. Moreover, hydrophilic surfaces are thought to be capable of antifouling. For example, surface with metal nanoparticles such as TiO2 has antifouling behavior, because the photocatalytic activities introduced by solar ultraviolet make the surface more hydrophilic so the biofilm is washed more easily [71]. However, some species exhibit different adhesion behavior on the same set of surface highlighting the importance of differences in cell-surface interactions [72] [73] Thus, it inspired the development of a surface that presents both hydrophilic and hydrophobic domains to settling cells and organisms. It has been shown that rougher surface increases adhesion of Pseudomonas [74]. In conclusion, the identification of effective antifouling topographies typically occurs through trial-and-error rather than predictive models, thus these theories are not sufficient to explain the real situation. Therefore, these formulas are not expected to guide the development of antifouling methods.

The 'attachment point theory' was first brought up by [74]It suggested that more attachment points during settlement resulted in higher and stronger attachment. It was reported that the settlement of different diatoms. The lowest settlement was found on microstructures with the feature wavelength slightly smaller than the size of fouling propagules/larvae (Figure 10), as only two points were available for attachment. With decreasing feature wavelength (Figure 10c→Figure 2-10b), the settlement increased with the increasing attachment points. Multiple attachment points were present when organisms settled on smooth surfaces (Figure 10a) or entirely inside the microstructure (Figure 10d, a microstructure big enough to host the entire organism), and the settlement was highly increased in this case. In the continuous work [75], the theory was further examined with more fouling species, i.e., the diatom Amphora sp., the green alga Ulva rigida, the red alga Centroceras clavulatum, the serpulid tubeworm Hydroides elegans and the bryozoan Bugula neritina. Generally, lower attachment of most tested organisms was observed on microstructures with the feature wavelength slightly smaller than the organism size. And the amount of settlement increased when the microstructures got wide enough to host one individual organism. Although it turned out that the theory was not confirmed for the settlement of non-motile algal spores of C. clavulatum, it strongly influenced the attachment of large macrofouling larvae (H. elegans and B. neritina) and also correlated with the attachment of small motile microfoulers (Amphora sp. and U. rigida). These findings reinforced the possible applications of the 'attachment point theory' in the field of biofouling to anticipate or even control the degree of fouling.

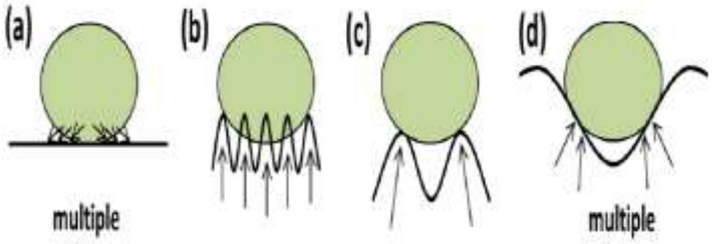


Figure 10 Schematic illustration of attachment points on topographies of different wavelengths (adapted from [74] (a) Multiple attachment points on the smooth surface; (b)-(c) fewer attachment points with increasing feature wavelength when the organism size is bigger than the microstructure size; (d) multiple attachment points when the organism fits entirely inside the microstructure

4.3 Challenges for physical antifouling methods.

The physical methods for prevention artificial surface from befouling organisms adhesion is not a most effective solution as antifouling, there are different antifouling theories to explained medication of surface topography, zeta potential topography.We can use physical antifouling methods in the combination of chemical methods

5 CONCLUSIONS

The biofilm formation on marine surfaces is the adsorption of an organic layer. In the biofilm formation, there are three stages, the Initial stage is fouling organism settled on the surface it's reversible stage, In stage second the biofouling organism multiply, they become more firmly attached and differentiate, changing gene expression patterns in ways that promote survival. In stage three, after firmly attached, the biofouling organisms begin to secrete a surrounding matrix. This is a protective matrix then forms an initial biofilm.

There are many methods to prevent the biofilm but these methods majorly divided into three categories chemical methods, biological methods and physical methods. In this review article, we majorly focus on chemicals methods to prevent the biofilm formation, in which we are interested in Non-toxic antifouling coating because this type of coating having good antifouling properties and not hazardous to marine biological life. Other methods as biological and physical can be used to prevent the biofilm formation, but they having same limitation and less long-term effect like chemical methods.

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