Application of functional polymer materials for marine anti-fouling

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Abstract. Marine organisms adsorb and grow on the surface of underwater facilities. This process, known as fouling, has a detrimental impact on marine shipping and development. Currently, in order to prevent marine biofouling, the most efficient and economical method is the application of antifouling coatings that synthesized by a diverse of different functional polymer materials. For this reason, this research will introduce the progress in five types of functional polymer materials, which are polymers with catechol groups, polysulfide-based polymers, polymer quaternary ammonium salts, hydrogels and silicone resin. Due to different functional groups properties as well as mechanisms of action, they have their own advantages in the application of antifouling coatings. Meanwhile, the future trend of antifouling coatings development and their application in real sea environment are prospected.

Keywords: anti-fouling; polymer; functional materials; marine environment; application

1. Introduction

Marine organisms often accumulate on immersed surfaces and underwater subjects, thus causing serious fouling problems. They can mainly be categorized into micro-organisms and macro-organisms [1], both of which settle on ship hulls. The marine environment is more vulnerable to fouling due to its specific chemical nature. It is not just an electrolyte solution, but a complex electrolyte system with high biological activity. Therefore, combined effects of corrosion and biofouling result in the formation of marine fouling.

Colonization of a new surface, composed of four phases, constitutes an overlapping time sequence. At the initial stage, organic molecules such as proteins, glycoproteins and some inorganic compounds collect on the surface of the substrate and form a thin layer. This process can occur within 1 minute of the substrate entering the water. Then, microorganisms such as bacteria and single-celled diatoms rapidly deposit on the basement membrane and bind to the surface via extracellular polymeric substances (EPS) to form a biofilm. After the formation of the biofilm, algal spores and protozoa are attached to the surface. At the final stage, large fouling macro-organisms (eg. barnacles, bryozoans, etc.), which are typically characterized by rapid reproduction and growth, start to grow on the surface. Not only can marine fouling increase the dynamic resistance of the tube walls and the ship's shell, it also increases the thermal resistance of the heat exchanger and leads to clogging of porous elements such as filters. Due to the unwanted development and the resulting substantial environmental and economic consequence, antifouling treatment is often deemed necessary in the marine environment [2].

In order to address the problem, three kinds of methods have been implemented to eliminate the negative effect, including biological, physical and chemical measures. Biological measures are based on the understanding and knowledge of the optimal habitat and the attachment mechanism of fouling organisms. The goal of anti-fouling is achieved through avoiding, interfering or interrupting the attachment process. Two main biological methods commonly used are circumvention of peak fouling and mixed culture. However, they are often highly selective and effective only for specific species. Physical measures are basically physical removal means to reduce or prevent the attachment of fouling organisms, including mechanical removal, exposure to sunlight and seawater filtration. A large amount of time and effort is required and therefore is of low efficiency and of high cost. Chemical measures are used to prevent the attachment of marine organisms by selecting effective

chemical substances to kill spores or larvae. They can be divided into drug immersion method and coating protection method.

The most commonly used is a combination of physical and chemical means. Among them, the most popular and effective one is anti-fouling coatings by using functional polymer materials. Traditionally, the application of cuprous oxide antifouling coatings is an effective way to forestall marine fouling. But when the concentration of dissolved organic carbon in seawater is high, the activity of free copper ions will be reduced, resulting in a decline in its antifouling ability. Furthermore, under the condition of H_2S in seawater, the cuprous oxide antifouling paint will also fail due to the generation of insoluble cuprous sulfide. In the 1960s, organic tin, organic lead, organic arsenic and other antifouling agents appeared, and their use with cuprous oxide played a synergistic role. However, the surface of these antifouling paints is rough and the toxic material is unstable, thus having an expiration date of only 2-3 years. Since the 1970s, organotin polymers with significantly improved anti-fouling effect were widely used as anti-fouling coatings for ships. However, because of the toxic effect to the marine ecosystem, organotin coatings are banned on ships worldwide. Since then, self-polishing coatings, biodegradable antifouling coatings and other environmentally friendly antifouling coatings have gradually become the focus of research and development.

There are two main categories of anti-fouling coatings, including the chemically active coatings and the non-toxic fouling release coatings, which are widely used on the market. The structure of polymer materials determines their properties, and the control and modification of the structure can obtain polymer materials with different characteristics. Compared to other materials, the unique structure of polymer materials with easy modification makes them obtain excellent properties that are irreplaceable. They are classified into low surface energy materials, amphiphilic polymers, antimicrobial agent grafted polymers, biomimetic antifouling materials, autogenous hydrogels, anti-protein adsorption materials, hydrolytic degradable polymers, biodegradable polymers, etc [3]. Hydrolytic degradation polymers can break their chains in the marine environment to achieve self-renewal, which is conducive to the controlled release of antifouling agents. The biodegradable polymer materials decompose under the dual action of water and enzymes. They are eco-friendly, surface self-renewal and have good mechanical properties. Furthermore, they can also be used as a slow-release system of antifouling agent, which is a promising class of marine antifouling materials.

Due to their unique properties, polymer coating materials are now widely welcomed and have been intensively researched. This research aims to give a brief introduction of the existing ways to prevent marine fouling through polymer modification with different functional groups, including catechol groups, polysulfide and quaternary ammonium salts.

2. Application of different functional polymers materials in marine anti-fouling

2.1. Polymers based on catechol groups

The catechol groups have universal adhesion properties and thus materials that consist of catechol groups results in highly adhesive antimicrobial materials. By synthesizing antimicrobial polymers containing catechol groups in branched chains and then anchoring the antimicrobial polymers to the surface of the substrate through the catechol groups, an antimicrobial and antifouling surface is produced. This method can be used to kill microorganisms without releasing biocides and losing biological activity. Antimicrobial polymers can be divided into passive and active polymers according to their antimicrobial principles. The process of colonization of a new surface is shown in Fig.1. Instead of coming into contact with bacteria, passive antimicrobial polymers rely on spatial resistance, electrostatic repulsion and low surface energy to prevent bacterial adhesion. Polyethylene glycols are the most common passive antimicrobial polymer materials based on the mobility of their long chains, their large volume repulsion and the site-blocking effect of their highly hydrated layers. The biofouling resistance of polyethylene glycol surfaces depends on surface density of the grafted polyethylene glycol. To construct high-density polyethylene glycol surfaces, multi-armed polyethylene glycols are of increasing interest [4].

In recent research, catechol groups have been used to obtain functionalized materials by loading metal nanoparticles onto the surface of substrates. For example, nano silver and dopamine were combined to produce highly effective antibacterial coatings. A polypeptide block copolymer was developed by Yoo et al. for surface coating through the combination of a protein-resistant polyinosinic acid (pSar) block with a dopamine-modified polyglutamic acid block. Silver nanoparticles (Ag NPs) were also incorporated into the copolymer [5]. Their experimental results showed that the antifouling properties of pSar blocks were better when the length of pSar blocks was shorter (probably due to the growth of chain length resulting in a lower graft density). The catechol group has two functions. It can act as an effective anchoring group on the metal oxide surface and induce the synthesis of Ag NPs. Based on such dual roles, pSar brushes and antimicrobial Ag NPs not only maintain a certain adhesion stability on the metal oxide surface, but also exhibit active antimicrobial activity and good biocompatibility.

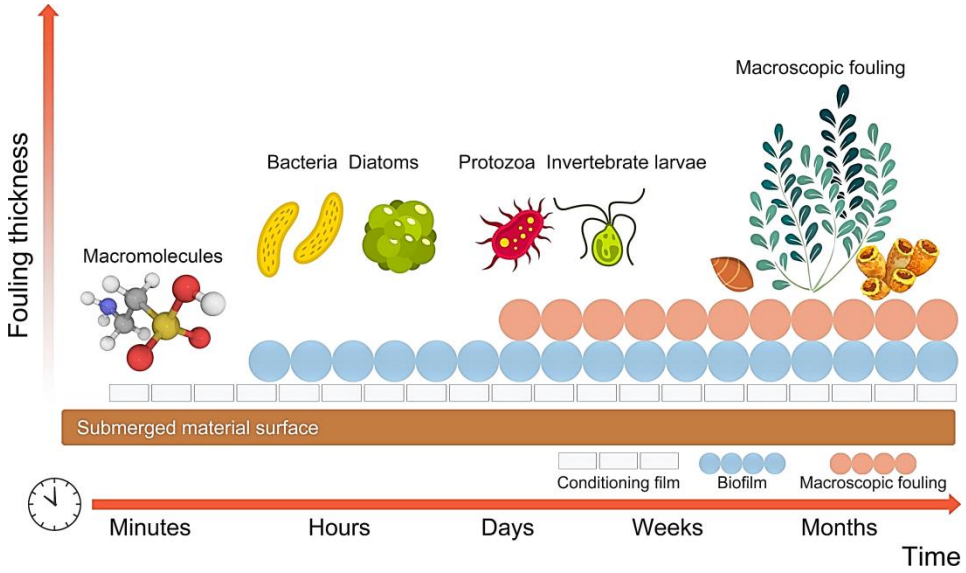


Fig 1. Process of colonization of a new surface [4]

2.2. Polymers based on polysulfide

Both amphiphilic polymeric antifouling materials and fouling detachment type antifouling materials are hot spots of antifouling materials at present [6]. However, traditional amphiphilic polymeric antifouling materials use polyethylene glycol hydrophilic chain segments, which are easily oxidized in the actual environment. This oxidation process affects the stability of the material and causes unsatisfactory interferences. Conventional silicone materials show good antifouling performance under high air speed, but their antifouling ability under static conditions is poor. They also have poor mechanical properties and weak bond strength with the substrate. To address the above problems, the poly (sulfuryl helium ester) can be used as the basis for chemical modification [7]. Fluorinated diols were introduced as side chains at room temperature to prepare fluorinated diol-modified poly (sulfuryl urethane) materials. This introduction of fluorinated diols solves the problem of easy oxidation. Meanwhile, a click reaction was used to combine silicone with polyurethane at room temperature to prepare silicone modified polysulfide ester. The modified compound has the mechanical properties and bond strength of polyurethane ester. It also demonstrates the hydrophobicity and low surface energy of conventional silicone material, as shown in Fig.2. To make further improvements on the static antifouling properties of silicone modified polysulfide materials, capsaicin, nano-silica particles and nano-zinc oxide particles were introduced by physical mixing in order to construct a silicone modified polysulfide/capsaicin with controlled release of capsaicin. A silicone modified polysulfide/silica with microstructure on the surface and a photocatalytic decomposition degradation of zinc oxide have low surface energy properties. It should be emphasized that experiments in real sea environment have been carried out and the results are positive. After 3.5-

month field immersion in seawater, less fouling material adhered to the surface of the sample with modified polysulfide coating. This indicated that during the 3.5-month static immersion, the coating maintained good antifouling ability. After 6 months of static immersion, although the sample was covered with a large number of fouling organisms, these organisms were more easily removed, indicating that it still had good antifouling ability [7].

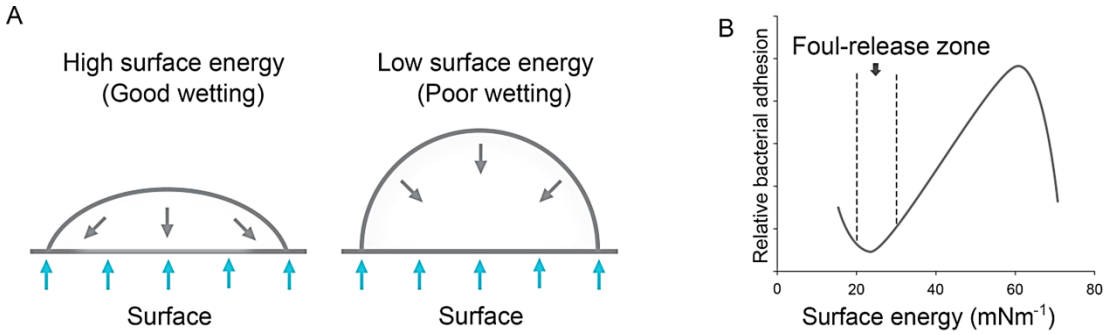


Fig 2. Low surface energy and foul-release [2]

2.3. Polymers based on quaternary ammonium salts

Polymeric quaternary salts are usually synthesized by introducing quaternary groups into polymer side chains, and the polymeric body can be polyvinylpyridine [8], polystyrene [9], polyacrylates [10] or polysiloxanes [11], etc. Polyacrylates are widely studied because of their flexible main chains. Furthermore, acrylate monomers can be copolymerized to change the hydrophobicity of the polymer and other structural characteristics. The replacement of the polymer backbone from acrylate to acrylamide can increase the polarity near the backbone and thus improve the biocompatibility of the polymer. There are many types of quaternary ammonium salts of acrylic or methacrylic acid-based polymers, which are used to improve antibacterial activity by changing charge density, hydrophobicity and molecular weight. Zhang et al. has discovered that as the type and length of substituted alkyl chains of small molecule quaternary ammonium salts change, their antibacterial activity also changes [7].

Polymer quaternary ammonium salts have strong hydrophilic macromolecule brush antifouling coating properties. The structure contains quaternary ammonium groups, which has a certain inhibitory effect on marine microorganisms. The basic bactericidal mechanisms are as follows: (1) Cationic bactericides adsorb to the surface of bacteria and penetrate their cell walls; (2) Bactericides damage cell membranes by binding to them; (3) Cellular materials leak, leading to bacterial death.

2.4. Hydrogels

Hydrogels are gel systems formed by hydrophilic polymers with a three-dimensional interconnected network structure that can swell but are insoluble in water [12]. They can be categorized into natural polymer gels and synthetic polymer gels. Natural hydrogels are mainly composed of natural polysaccharides or proteins, such as alginate gels, agar gels and collagen gels. Synthetic gels are formed by cross-linking and are classified into reversible physical hydrogels and stable chemical hydrogels [13]. The formation of physical hydrogels includes polymer chain entanglement as well as ionic and hydrogen bonding, as shown in Fig.3. Their formation and decomposition can be reversibly changed with physical conditions, and therefore are easily destroyed. Chemical hydrogel is a three-dimensional network gel formed by grafting or chemical cross-linking of macromolecules to produce new chemical bonds between macromolecules, and its cross-linked structure is an irreversible and stable gel, which can only swell but not dissolve [14] [15]. Synthetic hydrogels are mainly composed of polyethylene glycol (PEG), polyvinyl alcohol (PVAL), polyacrylamide (PAM), polyurethane (PUR) and acrylate polymers.

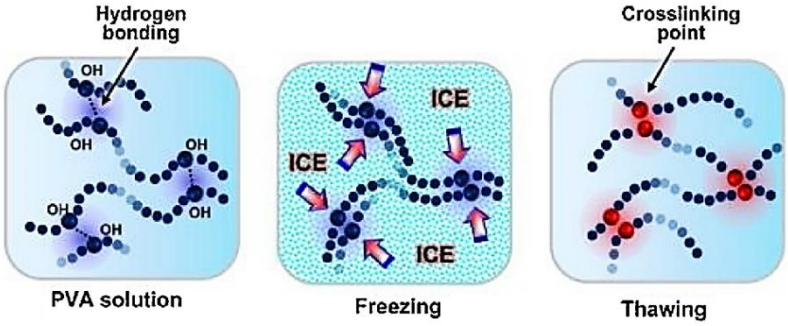


Fig 3. The principle of the preparation of hydrogels [13]

The hydrogel material inhibits the attachment of bacteria, thus effectively reducing the adsorption of proteins, polysaccharides and marine microalgae on its surface [3] [16]. The adsorption process of organic compounds, bacteria and marine microalgae on the surface of hydrogel is a key step in the fouling process. The formation of organic molecular layer and biological mucosa has considerable similarity and correlation. Many large marine organisms, such as whales and dolphins, are protected against fouling organisms by a hydrogel layer formed by the secretion of adhesive proteins on the body surface. Similarly, the dense layer of water molecules on the surface of hydrogel material and the unstable surface of this material due to low elastic modulus give hydrogel good anti-fouling ability, which can block the fouling phenomenon well from the root [17], as shown in Fig.4. Meanwhile, combined with the characteristics of easy modification of polymer compounds, the main chain of hydrogel polymer can suspend the antifouling agent with the tendency to avoid fouling biological effect, and gradually degrade and polish in seawater while giving the material surface special micro-morphology.

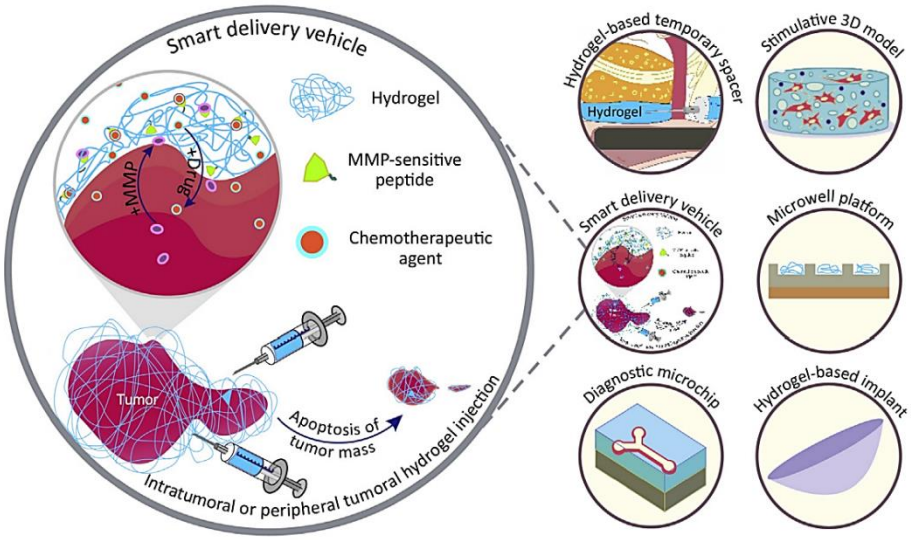


Fig 4. The application of hydrogels in different fields [17]

2.5. Silicone Resin

Silicones are organopolysiloxane, which can be divided into silicone oil, silicone resin and silicone rubber according to their molar mass and structure. Among them, silicone resin has great application prospects. Silicone resins are generally derived from hydrolytic condensation of silicone monomers and have the advantages of both inorganic and organic materials. The main chain of silicone polymer has repeating -Si-O-units. The Si-O bonds are longer than the usual carbon-carbon bonds, making the polymer chains more flexible [18]. Therefore, it is a very good kind of low surface energy material.

Silicone low surface energy antifouling coatings are formulated by adding color fillers, solvents, additives and suitable curing agents and catalysts with the above-mentioned film-forming substances as the base material. The antifouling mechanism of silicone resin is different from other materials.

The Bayer curve shows that the bond strength of low surface energy to fouling organisms is relatively low. To reduce the surface energy, the silicone polymer backbone can be rotated so that the methyl groups are enriched on the surface. The flexible structure with relative low surface energy enables the coating to obtain a smoother surface during the formation process, which facilitates the detachment of fouling organisms. In peel-off mode, hard organisms will detach from the coating surface easier and faster. In addition to superior fouling detachability, the silicone oxygen-bonded backbone gives silicone polymers good chemical stability and weatherability, resulting in a fouling life of more than 5 years.

However, the adhesion of silicone resin to the substrate is poor, so it is not effective as a film-forming material for antifouling coating alone and chemical modification is generally required. Modified silicone resins mainly use the hydroxyl group on the chain of polysiloxane to react with other compounds or active groups (such as hydroxyl, carboxyl, isocyanate, etc.) on polymers to produce resins with various properties [19]. Modified silicone resin overcomes the shortcomings of pure silicone resin and silicone rubber to achieve good application results. However, the introduction of a large number of non-low surface energy components into the molecule has greatly affected their low surface energy properties. So far, the series of coatings still have the disadvantages of poor recoat-ability and the need for regular dock cleaning.

3. Conclusion and perspective

Marine antifouling is an international challenge. As the level of research progresses, the polymers chosen by scientists to synthesize antifouling materials are changing. Currently, the main development goals of antifouling coatings are to achieve high energy efficiency, ease application, environmental friendliness and high stability. New biodegradable antifouling coatings have gradually replaced the traditional antifouling coatings for marine facilities. Non-toxic self-polishing antifouling coatings and bionic antifouling coatings containing natural active substances are gaining more and more attention. Based on this hot topic, this paper presents a discussion on the types of fouling organisms and the mechanism of biofouling formation, classifying them by the different functional groups of constituent polymers. Furthermore, their characteristics, formation mechanisms, current research progress and application prospects are described in detail.

The catechol group has good adsorption properties, enabling better stability on the surface of ship hulls and achieving better antifouling effect. Through passive and active antibacterial mechanism, it has better biocompatibility; Polysulfide based polymers are chemically modified at room temperature to eliminate its disadvantage of easy oxidation, thus enhancing its stability. At the same time, according to real sea study, it has been found that its antifouling ability is good. Quaternary ammonium polymers itself has a certain inhibitory effect on bacteria. By changing its side chain group type and length, their antibacterial ability will also vary. Hydrogels, due to its amphiphilic characteristics, can reduce the adsorption of organic matter and prevent the formation of biofouling layer. Meanwhile, hydrogels can easily degrade in the seawater environment to achieve the aim of environmental friendliness. Silicone resins have very low surface energy due to the deformability of the -O-Si- bond. Therefore, it can achieve better stability and have longer antifouling life.

At present, bionic antifouling technology has shown excellent antifouling performance and good development prospect, but the complex and diverse marine environment and the variety of fouling organisms make it difficult to achieve long-term antifouling by only one antifouling mechanism of bionic. As a result, the development of high-performance marine antifouling materials and related technologies is the focus of future research. Besides, due to a series of problems in experimental research, including poor material stability and high economic cost, the current applications are only in the laboratory stage and few commercial applications have been established. Therefore, more real sea research should be conducted in the future.

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