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Research Progress of Amphiphilic Polymer Marine Antifouling Coatings

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ABSTRACT
Marine biofouling not only increases ship resistance and energy consumption, but also corrodes Marine engineering equipment, causing huge economic losses and environmental hazards. Traditional anti-fouling coatings rely on toxic substances to achieve anti-fouling effects, which not only have a short service life but also are prone to cause Marine ecological pollution, which is not in line with the concept of green and sustainable development. Amphiphilic polymers, with their synergistic effects of hydrophilic and hydrophobic segments, can achieve efficient anti-fouling through physical and chemical mechanisms and have become a research hotspot in anti-fouling materials in recent years. This paper reviews the research and application of amphiphilic polymer antifouling coatings and looks forward to their future development direction, aiming to provide references for their further research and practical application.

KEYWORDS
Amphiphilic polymers; Antifouling coatings; Marine anti-fouling; Fluorine-containing materials

1 Introduction

Marine biofouling refers to the attachment and accumulation of microorganisms, animals, plants, etc. on the surface of the hull or underwater equipment, etc [1]. At present, Marine biofouling has caused a serious burden in terms of environment, ecology, safety and economy. Biofouling on the hull increases the weight and roughness of the hull, resulting in increased fuel consumption and greenhouse gas emissions. According to relevant data, Marine transport delays, hull cleaning and maintenance, the cleaning of desalination units, and biological corrosion caused by Marine biofouling result in an overall economic loss of more than $150 billion per year [2]. Traditional Marine antifouling coatings are characterized by the release of antifouling agents such as cuprous oxide, zinc oxide, and organotin to prevent the attachment of Marine organisms. It has a certain ability to resist Marine microbial adhesion, but the anti-fouling effect gradually decreases as the anti-fouling agent is continuously released, and the roughness of the coating surface increases, increasing frictional resistance and wasting fuel. Some of them also release toxic substances, causing serious harm to the water environment and Marine life [3-4]. Against this backdrop, the development of environmentally friendly, efficient and long-lasting anti-fouling coatings has become the current focus of research. Amphiphilic antifouling coatings refer to antifouling coatings with both hydrophobic and hydrophilic domains, whose surfaces not only have the soil-release properties of hydrophobic materials, but also have the highly effective resistance to protein adhesion of hydrophilic materials [5]. Fluorine-containing amphiphilic polymers, which combine the hydrophilicity and hydrophobicity of amphiphilic polymers, address the pain points of ordinary fluorine-containing coatings that rely solely on hydrophobic anti-fouling, are prone to adhering pollutants, and have a single self-cleaning ability. This paper focuses on amphiphilic polymer anti-fouling coatings, reviews key information, analyzes existing problems, looks forward to development trends, and provides references for their subsequent research and application.

2 Research on Antifouling Mechanisms of Amphiphilic Polymers

Amphiphilic polymers can be classified into various types based on their connection patterns and structural arrangements, among which amphiphilic block polymers and amphiphilic graft polymers are the most extensively studied [6-7]. Amphiphilic polymers have hydrophilic and lipophilic regions similar to those of surfactants. These amphiphilic polymers, which contain two parts with different solubilities and immiscible, form complex structures after phase separation and give the material special properties [8]. When the amphiphilic coating is immersed underwater, the hydrophilic segments migrate towards the coating surface and interact with the surrounding water molecules to form a hydrated layer on the coating surface, which greatly reduces the interaction between protein molecules and the material surface and decreases protein adsorption; At the same time, the coating surface still maintains the low surface energy of the hydrophobic material, reducing the adhesion strength of fouling organisms and making them easy to be washed away by water flow, thereby preventing fouling organisms from adhering (Figure 1) [9-10].

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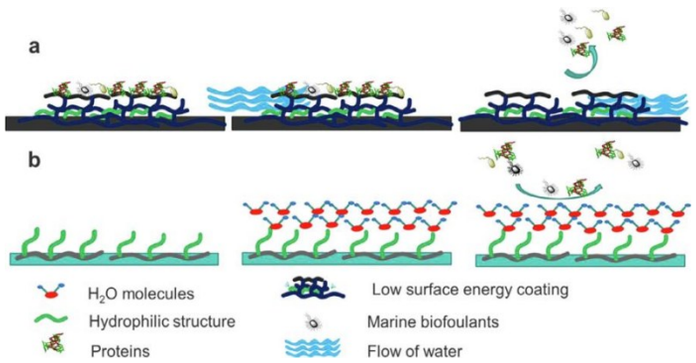

Figure 1 Anti-fouling mechanism of the amphiphilic coating. (a) low surface energy antifouling mechanism, (b) hydrophilic antifouling mechanism [11]

Guo et al. [11] functionalized a highly hydrophilic polymer polyvinylpyrrolidone (PVP) with triethoxysilane to form an amphiphilic coating directly crosslinked with PDMS at room temperature. The results showed that the hydrophilicity of the modified PDMS matrix was significantly enhanced. In addition, compared with the original PDMS coating, the PDM-PVP coating can effectively prevent the adhesion of bacteria and Navicula diatoms, as well as resist the attachment of simulated barnacles, and also demonstrated excellent anti-biological contamination performance for at least 4 months in actual sea area tests. The strong hydrophilicity of PVP and the low surface energy of PDMS are the main reasons why this amphiphilic antifouling coating has good resistance to biofabrication.

Su et al. [12] prepared a new type of amphiphilic coating with micro-nano structures by arranging hydrophobic and hydrophilic components to control assembly and phase separation during polymer crosslinking and local swelling processes. Based on polyethylene glycol, amphoteric ions and hydrophobic components, the coating reduced the entropy and enthalpy driving forces for the adsorption and sedimentation of Marine microorganisms, while the amphoteric ions could form a thin water layer to prevent the attachment of Marine microorganisms (Figure 2). Experimental results show that the coating has good mechanical stability, greatly expanding its application range and service life, and can significantly reduce the attachment of seaweeds and barnacles in the ocean.

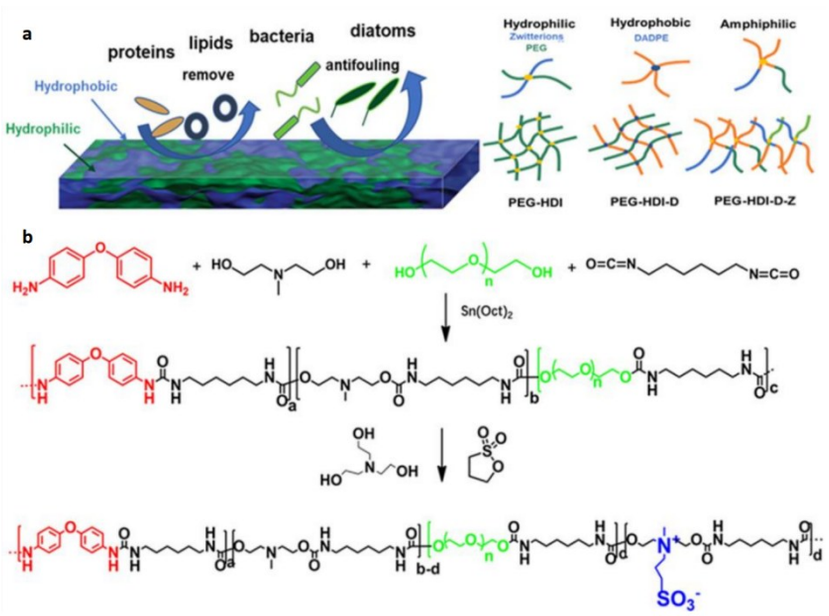

Figure 2 (a) Schematic diagram of Marine anti-fouling mechanism; (b) Synthesis of polyurethane coatings [12]

3 Amphiphilic Fluoropolymer Antifouling Materials

Fluoropolymers are pore-free, low critical surface energy materials (10-20 mN/m), and their low surface adhesion results from exposed -CF_3 groups in the polymer. The size of the compound's surface energy decreases as the density of the fluorinated chemical groups on the surface increases [13]. During the film formation process, the perfluoroalkyl chains of this type of polymer migrate towards the surface and form a closely packed state, thereby minimizing the surface energy. Because fluoropolymers have a smooth surface and low surface energy, only weak interactions are formed

between Marine organisms and the coating [14]. Polytetrafluoroethylene (PTFE) was initially regarded as a promising alternative material for fouling release because of its low surface energy, but its surface is easily scratched by hard fouling, and the high local polarity of the carbon-fluorine bonds on the coating surface allows barnacles to adhere tightly to its surface. The irregularity of the surface allows the bio-binder to invade and solidify in the microcavities and create a strong mechanical interlock [14]. Compared with silicone coatings, fluoropolymer coatings require higher shear force to remove fouling organisms from their surfaces. In addition, fluoropolymers undergo rapid recombination in seawater, which weakens their hydrophobicity and fouling release properties [15].

Therefore, combining the properties of fluoropolymers with those of amphiphilic polymers can make the anti-fouling effect more comprehensive. Hydrophilic groups can form a hydrated layer that hinders the initial attachment of proteins and microorganisms; The hydrophobic fluorine groups lower the surface energy, making it easier for the attached dirt to be washed away by seawater, creating a "double protection". In addition, the hydrophobic layer of ordinary fluorine-containing coatings is prone to damage after prolonged immersion, resulting in the failure of the anti-fouling effect; The synergistic effect of the amphiphilic structure can slow down the aging of the coating, extend the anti-fouling period, reduce maintenance costs, and thereby enhance its durability.

Tang Xinde et al. [16] synthesized fluoropolymers of polyethylene glycol-polystyrene-perfluorohexyl ethyl acrylate (PEG-b-(PS-b-PFHEA)$_4$) by atomic transfer radical polymerization (ATRP) technology. Nuclear magnetic resonance hydrogen spectroscopy (1H-NMR) and gel chromatography (GPC) characterizations indicated that The polymer has a microphase separation function, which leads to self-assembly and inhibits the attachment of Marine organisms, making it suitable as an antifouling material.

Amphiphilic grafted polymers can have good structural symmetry, with both rigid molecular bonds and flexible molecular chains in the molecular structure, so polymers have unique physical and chemical properties. J F Hester [17] prepared amphiphilic graft copolymers directly from commercial poly (vinylidene fluoride)(PVDF) using the Atom Transfer Radical Polymerization (ATRP) method. They found that the direct initiation of the secondary fluorination sites of PVDF facilitated the grafting of hydrophilic copolymer monomers. PVDF amphiphilic graft copolymer derivatives with poly (methacrylic acid) side chains (PVDF-G-PMAA) and poly (oxyethylene methacrylate) side chains (PVDF-G-POEM) were prepared using this method. The surface separation of the PVDF-G-POEM additive in PVDF is the cause of wettable, antifouling surfaces on PVDF filter membranes. When the bulk POEM concentration of the PVDF/ 5wt% PVDFg-POEM membrane is 3.4 wt%, the near-surface POEM concentration is 42wt%, showing strong anti-fouling ability.

Zhang Guangfa et al. [18] prepared amphiphilic block copolymers by copolymerizing the hydrophobic low surface energy fluorine-containing compound C_6SMA and the hydrophilic monomer PEGMA, which has been proven to have good protein adsorption inhibition performance. A series of amphiphilic fluorine-containing block copolymers P(PEGMA-co-MMA)-b-PC_6SMA with different structural compositions were successfully prepared by RAFT polymerization first. The wettability, surface chemical composition and surface morphology of the dynamic surface of the amphiphilic copolymers were characterized by surface contact Angle, XPS and AFM respectively, and finally the anti-protein adsorption test of the copolymer film surface was conducted using fluorescein isothiocyanate labeled bovine serum albumin (BSA-FITC). The results show that the copolymer film surface is an amphiphilic dynamic surface with both hydrophilic and hydrophobic components, and the two components jointly determine the wetting performance and surface energy of the surface. The study also found that the amphiphilic fluorine-containing block copolymer membranes have excellent performance in inhibiting protein adsorption. The analysis suggests that the microphase separation structure on the block copolymer surface and the surface recombination occurring in the water environment are the main reasons for its excellent antifouling performance.

4 New Type of Environmentally Friendly Amphiphilic Polymer Antifouling Coating

While traditional Marine antifouling coatings play a certain role in antifouling, they also bring certain toxic effects to the Marine environment and Marine life. Compounds such as arsenic and mercury were used as antifouling agents in early Marine antifouling coatings, but they were phased out because of their excessive toxicity [19]. Then came soluble antifouling coatings with cuprous oxide as the antifouling agent base, followed by insoluble antifouling coatings with high copper compounds (with polymers as the main base), organotin and organotin-cuprous oxide composite toxic antifouling coatings, and then high-performance, long-lasting, and excellent construction performance organotin self-polishing antifouling coatings (SPC), A big step forward in antifouling coatings technology. Although SPC anti-fouling coatings have both anti-fouling and drag reduction effects, they are highly toxic because they contain tin. It causes serious Marine pollution after release [20]. Studies have shown that seawater with organotin content higher than $0.1x10^{-6}$ will affect the Marine ecological environment, seriously affect the growth and reproduction of Marine organisms, and cause genetic variations in Marine organisms. With the growing call for environmental protection, coastal countries have enacted laws to restrict the use of organotin [21].

Although low surface energy materials such as fluoropolymers and amphiphilic fluoropolymers have many advantages, they release fluorinated compounds (such as perfluorooctane sulfonic acid, etc.) over a long period of use. These substances are chemically stable, difficult to degrade naturally in the ocean, accumulate in aquatic organisms, and even affect ecosystems and human health through the food chain Some substances have been listed as environmental priority control pollutants [22]. And the fluorine-containing raw materials themselves are expensive, and the coating preparation process is complex, resulting in the product cost being much higher than that of ordinary resin-based antifouling coatings; At the same time, its application imposes strict requirements on substrate treatment and coating environment, further increasing the overall cost of the project. Therefore, the development of new non-toxic antifouling coatings that do not pollute the environment to replace traditional toxic antifouling coatings has become an inevitable trend, and research on environmentally friendly Marine antifouling coatings has also become increasingly popular.

Yin Zhaoyi [23] et al. reacted hexafluorobutyl acrylate (HFBA) with n-acryloimoline (ACMO) to obtain an amphiphilic initiator, and then used the amphiphilic polymer to initiate the ring-opening polymerization of caprolactone to prepare the amphiphilic degradable polymer P(HF_x-AM_y) -CL_z. The amphiphilic segments on the main chain give the coating excellent anti-protein adsorption ability by enrichment on the surface of the coating, which limits the initial formation of Marine fouling, and also gives the coating excellent anti-algal adhesion performance. The presence of the amphiphilic components also limits the crystallization of the polyester segments within the system, addressing the issue of high system crystallinity in related polyester materials

The problem of poor overall performance. The coating has good adhesion to the substrate and maintains stability underwater. This material does not require the addition of antifouling agents and is a green and environmentally friendly antifouling material with promising application prospects in Marine antifouling.

Li Yi [24] et al. synthesized a series of well-defined EB and capsaicin copolymers (PEB-co-PAMM) with controllable molecular weight and composition through free radical polymerization (Figure 3a). PEB-co-PAMM was conveniently covalent grafted onto the PDMS network via terminal siloxane (Figure 3b). PEB-co-PAMM can effectively kill bacteria, hydrolyze to CB and acrylic acid copolymer (PCB-co-PAA) in weakly alkaline seawater, release the killed bacteria and resist the formation of Marine slime. Meanwhile, the natural capsaicin derivative Paeonol on the side chain can also be continuously released to repel Marine fouling organisms (Figure 3b).

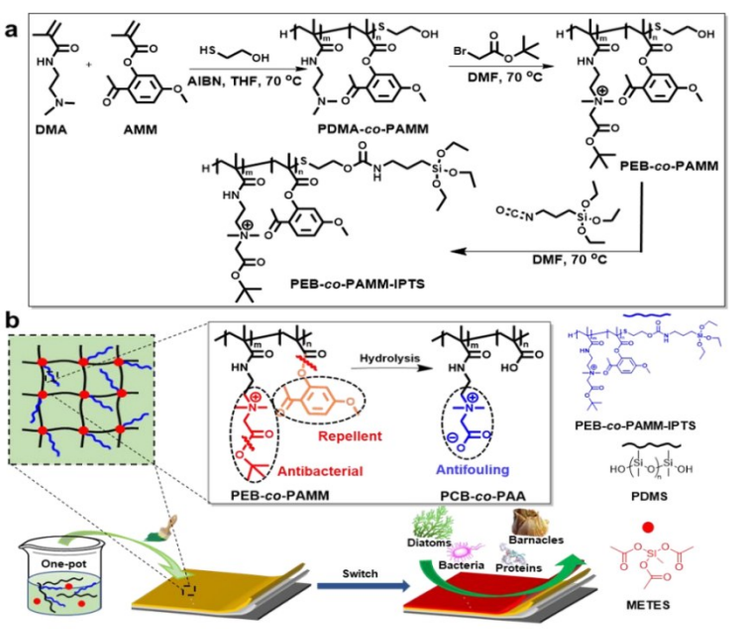

Figure 3 Schematic diagram of base coatings [24]

(a) synthetic route of EB and capsaicin copolymer; (b) Graft-convertible EB and capsaicin copolymer PDMS

5 Summary and Outlook

Marine biofouling is harmful. Traditional anti-fouling coatings rely on toxic substances, which pollute the environment and have a short lifespan. Amphiphilic polymer antifouling coatings have become a research hotspot due to the synergistic action of hydrophilic and hydrophobic segments. The hydrophilic segments form a hydrated layer to prevent protein adsorption, and the hydrophobic segments have a low surface energy to help dirt be washed away. Fluorine-containing amphiphilic polymers can also achieve "double protection". However, fluorine-containing materials have

problems such as difficulty in degradation, high cost and strict construction requirements, which have driven the development of new environmentally friendly coatings, such as degradable polymers and natural substance modified coatings, showing good prospects. In the future, the design of amphiphilic polymer structures needs to be further optimized to enhance the mechanical stability and long-lasting anti-fouling performance of the coating; Develop low-cost, easy-to-apply fluorine-free environmentally friendly formulations and promote industrialization; Strengthen long-term performance tests in actual sea areas and combine multi-disciplinary technologies to facilitate their wide application in Marine engineering and achieve the goal of green pollution prevention.

References

[1] Rahaman, M. S., Therien-Aubin, H., Ben-Sasson, M., et al. (2014). Control of biofouling on reverse osmosis polyamide membranes modified with biocidal nanoparticles and antifouling polymer brushes. J. Journal of Materials Chemistry B, 2: 1724-1732.

[2] Nurioglu, A. G., Esteves, A., & de With, G. (2015). Non-toxic, non-biocide-release antifouling coatings based on molecular structure design for marine applications. J. Journal of Materials Chemistry B., 3: 6547-6570.

[3] GUI Taijiang. (2005). The current situation and development trend of Marine antifouling coatings. J. Modern Coatings and Painting, 5: 28-29.

[4] Hellio, C., Broise, D. D. L., & Galy, L. (2001). Inhibition of marine bacteria by extracts of macroalgae: potential use for environmentally friendly antifouling paints. J. Marine Environmental Research, 52,: 231-247.

[5] Zhou, Z., Calabrese, D. R., Taylor, W., et al. (2014). Amphiphilic triblock copolymers with PEGylated hydrocarbon structures as environmentally friendly marine antifouling and fouling-release coatings. J. Biofouling, 30: 589-604.

[6] Oda, Y., Kanaoka, S., Sato, T., et al. (2011). Block versus random amphiphilic copolymers as antibacterial agents. J. Biomacromolecules, 12: 3581-3591.

[7] Hester, J. F., Banerjee, P., Won, Y. Y., et al. (2002). ATRP of amphiphilic graft copolymers based on PVDF and their use as membrane additives. J. Macromolecules, 35: 7652-7661.

[8] Zhou Ying. (2016). Synthesis and phase study of amphiphilic polymeric polymers. D. Beijing University of Chemical Technology, Beijing.

[9] Patterson, A. L., Wenning, B., Rizis, G., et al. (2017). Role of backbone chemistry and monomer sequence in amphiphilic oligopeptide- and oligopeptoid-functionalized PDMS- and PEO-based block copolymers for marine antifouling and fouling release coatings. J. Macromolecules, 50: 2656-2667.

[10] Barletta, M., Aversa, C., Pizzi, E., et al. (2018). Design, manufacturing and testing of antifouling/foul-release (AF/FR) amphiphilic coatings. J. Progress in Organic Coatings, 123: 267-281.

[11] Guo, H., Yang, J., Zhao, W., et al. (2019). Direct formation of amphiphilic crosslinked networks based on PVP as a marine anti-biofouling coating.J. Chemical Engineering Journal, 374: 1353-1363.

[12] Su, X., Yang, M., Hao, D., et al. (2021). Marine antifouling coatings with surface topographies triggered by phase segregation. J. Journal of Colloid and Interface Science, 598: 104-112.

[13] Shafrin, E. G., & Zisman, W. A. (1967). Critical surface tension for spreading on a liquid substrate. J. The Journal of Physical Chemistry, 71: 77-83.

[14] Perez, M. C. (2009). Advances in marine antifouling coatings and technologies. J. 554-571.

[15] Zhu, P., Meng, W., & Huang, Y. (2017). Synthesis and antibiofouling properties of crosslinkable copolymers grafted with fluorinated aromatic side chains.J. RSC Advances, 7: 3179-3189.

[16] Tang Xinde, Han Nianfeng, Zhou Dejie. (2008). Synthesis and Characterization of Fluorine-containing amphiphilic Antifouling polymers. J. Modern Chemical Engineering, S2: 197-199.

[17] Hester, J. F., Banerjee, P., Won, Y. Y., et al. (2002). ATRP of amphiphilic graft copolymers based on PVDF and their use as membrane additives.J. Macromolecules, 35: 7652-7661.

[18] Zhang G F. (2013). Preparation of amphiphilic fluorine-containing block copolymers and their surface and antifouling properties. D. Zhejiang University, Zhejiang.

[19] Jin X H. (2006). Marine fouling organism control technology and development (III). J. Materials Development and Applications, 21: 44-46.

[20] Pan Shanshan. (2017). Research on cationic polyelectrolyte Antifouling coatings with functional conversion mechanism.D. Harbin Institute of Technology.

[21] Peres, R. S., Baldissera, A. F., Armelin, E., et al. (2014). Marine-Friendly Antifouling Coating Based on the Use of a Fatty Acid Derivative as a Pigment.J. Materials Research-Ibero-Aamerican Journal of Materials, 17: 720-727.

[22] Li X. (2007). The environmental and health hazards of perfluorinated compounds such as perfluorooctane sulfonic acid and perfluorooctanoic acid have drawn great attention from the international community. In: Proceedings of the Annual Conference of the Chinese Society for Environmental Sciences (2007). Beijing. pp. 1082-1089.

[23] Yin Z Y. (2021). Preparation and performance study of Amphiphilic biodegradable polyester coatings. J. Coatings Industry, 51:9-16.

[24] Li Y. (2022). Zwitterionic polymer-modified PDMs-based Marine antifouling coatings. D. Tianjin University, Tianjin.