

Original Paper

Research Progress and Prospect of Marine Antifouling Coatings

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Abstract

Marine biological pollution refers to activities such as a large number of barnacles, algae and other organisms or microorganisms gathering and damaging ships or other marine industries. Among them, the most effective way is to use degradable materials as the substrate and add antifouling agents that can destroy fouling organisms. Traditional marine antifouling coatings release toxic substances with broad spectrum, such as cuprous oxide and organotin, so as to achieve effective antifouling. However, with the adverse effects on the marine environment, it is a long way to go to study and prepare environment-friendly antifouling agents. This paper mainly introduces the traditional degradable materials PCL, PLA, etc., and also introduces the current low-toxic antifouling agent DCOIT composite materials and new natural antifouling agents, etc.

Keywords

Marine antifouling coatings, Natural antifouling agent, Environmentally friendly

1. Introduction

The most important transportation mode in international logistics is ocean transportation. It refers to the way of shipping goods between different countries and regions. Marine fishing is an industry that uses ships to catch marine fish and other aquatic animals in coastal, offshore and offshore waters. Whether it is marine transportation or fishing operation, its ship equipment and instruments run underwater for a long time, so that a large number of parasites such as algae or barnacles that damage the hull are attached to the surface. This leads to the decline of ship safety, and the increase of hull weight leads to the substantial increase of transportation costs such as fuel consumption. It has seriously affected the development of marine transportation, marine fishing and other industries. Most of the traditional self-polishing antifouling coatings contain toxic substances or antibacterial agents as fillers, and the purpose of antifouling is achieved by releasing toxic substances. Therefore, in recent years, researchers

have devoted themselves to exploring environmentally friendly and harmless antifouling technologies. In this paper, a new prospect and analysis of antifouling coatings with new development potential are put forward.

2. Research on Marine Biofouling Hazards and Formation Processes

2.1 Marine Pollution

The oceans cover about 71% of the earth's surface and are rich in natural resources, including biological, energy and mineral resources. Land is growing. The ocean plays an important role in the future economic life. However, in the case of long-term submergence of marine facilities such as ships, offshore oil drilling platforms, nuclear power plants, terminals and other marine facilities, in addition to the problem of seawater erosion, the phenomenon of marine biological pollution (Ye & Chen et al., 2017). Marine plants have had something detrimental to all the industries that have operated at sea since then. For a long time which includes economic, environmental and safety. Another major danger associated with marine pollution is the destruction of coatings and accelerated plant corrosion. Rotor tanks have a strong bond with the shell through biological adhesives, whose growth gradually penetrates the coating, damaging it and leading to corrosion. Contaminated organisms also increase the frequency of cleanups, replacement of marine coatings on the site and repairs, which leads to projected costs. Discounts. In addition, contaminated marine organisms block the pipelines of marine installations, reducing pipelines, lowering flow and reducing operational efficiency ratios. Marine resources are abundant and countries are increasingly focusing on the utilization of marine resources. Problems and Losses Associated with Plant and Animal Pollution Marine Corps. Therefore, addressing marine pollution is critical to the economy, the environment, and human health.

“Marine pollution” refers to biological contamination caused by the persistent adhesion and growth of various marine organisms on the surface of facilities that have been immersed in seawater for a long period of time. There are about 4,000 to 5,000 species of contaminated marine organisms that can be categorized into two main groups. Categories: contaminated microorganisms and macro-organisms. Macro-contaminated organisms can be divided into soft and contaminated organisms. Hard contaminated microorganisms consist mainly of mononuclear cells such as bacteria, glycospores, and protozoa. Heavily contaminated soft organisms consist mainly of visible algae such as seaweeds and invertebrates such as corals, sponges, sunflowers, and hydraulics. And other large cetaceans are mainly crustaceans invertebrates, such as rotor tanks, molds and so on.

2.2 Risks of Marine Biological Pollution

The risk of marine biological pollution can be divided into three main categories:

- (1) Accelerate metal corrosion. Certain corrosive organisms destroy the coating on the surface of the metal, so that the metal is exposed to corrosion; through photosynthesis to produce oxygen to increase the concentration of oxygen dissolved in the water, accelerating the corrosion of the metal.
- (2) Impairment of normal use of facilities, attachment of contaminated organisms increases the strength

of ships, reduces sailing speed, and increases the consumption of hydrocarbons for normal use; Impact on aquaculture production and quality. L'adsorption of contaminated organisms affects the normal growth of shells, such as oysters, which in turn reduces their growth. Production adhesion of contaminated organisms to algal surfaces affects the quality of algal products.

2.3 Processes by which Marine Biofouling Occurs

When clean and non-toxic materials are immersed in seawater, thousands of marine organisms colonize the surface of the material, competing for their respective life cycles and becoming generalized into the biota. The marine biodegradation process consists of several key steps: first, the formation of a film organic first, adsorption of soluble organic substances, such as sea water-soluble proteins, polysaccharides or glycoproteins, as well as inorganic materials are physically adsorbed on the surface of the material, and then the accumulation of an organic film within a few minutes. Time proteins and other metabolic products produced primarily by biological release sailor organic membranes with a negative surface and a thickness of about 15 mm, affecting some of the initial properties of the material surface (e.g., polarity and density of the surface fill, hydrophobicity, etc.), while creating an environment conducive to the growth of microorganisms such as 'sources'. The microorganisms, such as bacteria, isolates, and protozoa, that food next grows on organic membranes, begin to secrete extracellular metabolites ("EPS") that slowly accumulate to form microbial membranes, which are dependent on "low van der Waals forces", hydrogen bonding, or electrostatic effects, and thus these methods are reversible; microbial membranes are component organic have a variety of microorganisms and their own secreted EPS, which create favorable environments for the continued growth of microbial larvae, algal spores, and contaminated macroorganisms. The biological species in the membrane rapidly transforms from microorganisms to a complex biological community that includes macro-contaminated organisms and microorganisms, and finally, the width of the organisms attached to the surface of the membrane begins to evolve, the surface and thickness begins to evolve. The contamination is increasing and eventually becomes a variety of complex, contaminated biomes (Yang & Dong et al., 2019).

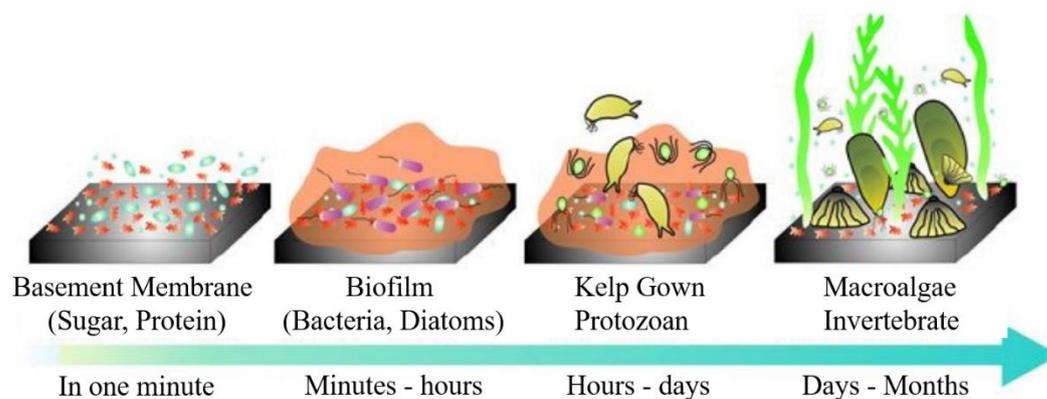


Figure 1. Marine Fouling Formation Process

3. Types of Antifouling Coatings

3.1 Degradable Materials

Degradable self-polishing antifouling coating is the addition of degradable substances to the coating, and its environment-friendly property attracts a large number of researchers' research. At present, the traditional polyester polylactic acid (PLA) and polycaprolactone (PCL) can be hydrolyzed in the marine environment, and the surface fouling organisms can be removed by renewing the surface to achieve the purpose of self-polishing. Ma Chunfeng et al. developed a series of biodegradable polymer pollution control materials and successfully applied them to marine experiments for the first time (Yao, Chen, & Ma et al., 2014). Sung Hyun Kwon used tributyltin self-polishing coating (TBT-SPC) in the resistance to marine pollution and it has been widely utilized and researched with great success (Ma & Liu et al., 2016).

Polylactic acid (PLA) is a completely biodegradable material, which is widely used in food, medicine and other fields because of its non-toxicity, antibacterial, inertness and biocompatibility. Because of the uncontrollable degradation efficiency, PLA must be improved to obtain controllable degradation efficiency and good performance materials. Polycaprolactone (PCL) is a degradable polymer material, which is currently used as an antifouling paint component that can be degraded in seawater. However, due to its high crystallinity, the hydrolysis rate is slow. It is necessary to add the prepared composite material to improve the hydrolysis speed and performance.

Yao team physically mixed PCL with clay (kaolin) to prepare PCL/ clay composites (Sung & Inwon, 2020). In which the ingredients of DCOIT antibacterial agent are added. Experiments show that the existence of clay reduces the size of PCL spherulites and increases the degradation rate. At the same time, the coating can be controlled to inhibit the explosive release of the antibacterial agent, so that the antifouling agent can be released at a relatively stable and effective rate. However, the addition of clay also has an adverse effect on the composite material, and seawater immersion leads to cracks on the surface of the coating. Finally, the composite material only has a life of 10 months in seawater. Compared with pure PCL coating, the mechanical properties of the composite coating are somewhat reduced.

3.2 Antifouling Agent

Traditional antifouling coatings use physiological toxicity, that is, use antifouling agents with broad-spectrum antifouling property to kill marine organisms on the surface. At the same time, however, it brings serious environmental pollution and the accumulation of toxins in marine organisms that destroy the ecological balance. Joana Figueiredo pointed out that the broad spectrum of DCOIT poses a threat to the ecosystem (Joana, Susana, & Roberto, 2020). This species constitutes a potential damage to ecosystem functions and interferes with other metabolic pathways. Jesus Dipo Paixo Silva de team studied the acute and chronic effects of fungicides containing DCOIT on tropical marine micro-crustaceans, and pointed out that the toxicity of DCOIT was far greater than that of compound SiNC-DCOIT-Ag (Jesus, Figueiredo, Maia, Martins, & Nilin, 2021). At the same time, experiments

show that the compound has little risk to the environment, but it still has great toxicity to non-target tropical mysis.

3.3 Natural Antifouling Agent

Since the use of toxic chemicals such as organotin was banned, many environmental-friendly biological antifouling agents have been developed and applied to marine antifouling coatings. Since 1980s, a new bionic antifouling agent from nature has become a breakthrough for researchers to solve the environmental problems of antifouling coatings. For example, a component extracted from natural plants and animals is used as an anti-fouling agent to replace the toxic component in the anti-fouling agent. Hui isolated four glycoside compounds from the widely distributed plant oleander, and tested their anti-barnacle growth activity (Hui, Chen, & Guo et al., 2018). The evaluation showed that the compounds had strong anti-barnacle attachment ability. At the same time, it is suggested that oleander extract has some moderate and low toxicity to non-target organisms. This shows that the glycoside compound extract from oleander has a good application prospect and commercial value as a natural antifouling agent. Tian Limei disclosed an environment-friendly marine antifouling component coffee. The silicone resin and coffee are made into composite excipients, which will effectively interfere with the formation of fouling biofilm in the initial stage of growth and prevent fouling organisms from multiplying and attaching in large quantities (Tian, Jin, Wang, Yin, Shang, Zhao, & Sun, 2021). Zhou (2008) studied the environmentally friendly algae inhibitor. Among them, the comparison of the effect and the ability of algae inhibition of traditional Chinese medicine, garlic and tea was mainly studied. The results showed that ebony, coptis chinensis, rhubarb, green tea and other materials had inhibitory effect on *Alexandrium tamarense* DH01. Furthermore, the combination of *Radix Isatidis*+*Radix Sophorae Flavescentis*, *Radix Isatidis*+*Herba Houttuyniae*, etc. was further studied, and it was found that it had a certain effect on inhibiting algae.

4. Summary

With the enhancement of human's awareness of marine environmental protection and the deterioration of marine ecological environment, it is one of the important fields of marine antifouling development to study and prepare environment-friendly antifouling coatings with low toxicity and no toxicity. Degradable materials and effective antifouling agents are important components in antifouling coatings. Therefore, the extraction and synthesis of natural antifouling components in nature is one of the research hotspots. It is also necessary to constantly discover novel environment-friendly anti-pollution ingredients such as coffee, traditional Chinese medicine and so on. Traditional Chinese medicine is the product of the Chinese nation's thousands of years, and it has made great achievements in many fields. Through research and study, I think that Chinese medicine, as a natural antibacterial component, may be used in marine antifouling coatings. It can effectively inhibit the formation of biofilm at the initial stage of growth, but its practicability, stability and compatibility need further experiment and research. It is believed that with people's research on the attachment molecular mechanism of fouling organisms

such as barnacle larvae and the continuous improvement of the technology of separating and extracting pure natural antifouling components. The degradable antifouling coatings of compound natural antifouling agents will tend to mature. So as to reduce marine pollution, reduce the anti-pollution cost of marine activities and realize further comprehensive application.

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