Original Paper

Process Study on the Preparation of Degradable Antifouling

Paint Coatings by Solvent Method

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Abstract

Marine anti-fouling coatings have been widely used as one of the effective methods to prevent marine fouling organisms from adhering to the surfaces of various marine facilities. The main types are self-polishing anti-fouling coatings and low surface energy anti-fouling coatings, and biomimetic antifouling paint. Due to the increasing awareness of environmental protection, the anti-fouling coatings harmful to the environment have been gradually banned, so the research and development of new anti-fouling coatings has become the primary direction of development.

In this paper, polycaprolactone and PLA were used as resin base materials, capsaicin as bio-friendly anti-fouling agent, starch as polysaccharide additive, the experimental samples were prepared by adjusting the mixture ratio of these materials. The experiment of adding starch and unadded starch was carried out by using Magnetic stirrer and other experimental equipment to simulate the hanging board method on the sea and observed and recorded, the effect of Starch on the hydrolysis of anti-fouling coatings using single component or blends of biodegradable materials such as polycaprolactone, polylactic acid (PLA) as resin matrix was investigated.

The results showed that starch could promote the hydrolysis of resin-based materials such as PCL, and the solubility of PCL and PLA in chloroform was obtained, a preparation method of antifouling coating for marine static culture equipment was obtained.

Keywords

Marine antifouling coatings, bionics, environmental protection, polycaprolactone, polylactic acid

1. Introduction Section

1.1 Introduction

Nowadays, human's marine activities are becoming more and more frequent, among which, how to solve the problem of marine fouling has been troubling us. The general definition of marine fouling refers to the growth and reproduction of marine organisms on the surfaces of ships, marine utilities, fishery equipment, etc., which are submerged in seawater. This can damage and render marine equipment unusable, causing huge economic losses to us. Humans have come up with many ways to deal with this problem, among which the use of anti-fouling coatings on the surface of marine equipment is one of the most economical and common methods. Some anti-fouling coatings can protect the marine equipment from erosion, but they may have a certain degree of adverse effect on the marine environment. The specific attachment activities of marine organisms is a very complex process, scientists through the specific activities of marine organisms attached to the behavior and its impact on the biological attachment of various factors for in-depth study, so that we have a certain degree of basic scientific understanding of the specific attachment mechanism of marine organisms. Effective prevention and control of marine biofouling hazards, how to realize not to damage the environment and to improve the anti-fouling performance have received more and more attention. The present study is on the coating of bionic anti-fouling materials.

1.2 Development of Marine Antifouling Materials

1.2.1 The Formation and Harm of Marine Fouling

Marine fouling, generally refers to the ocean some animals, plants, microorganisms attached to the shell of marine equipment, such as ships, submarine pipelines, fishing gear, etc., will increase the weight of the hull of the ship, obstacles to the navigation of the hull, increase fuel consumption. At the same time, it will also cause serious corrosion of the shell, which will cause great economic losses for marine activities.

The formation of marine fouling usually needs to go through four stages.

Stage 1: Within minutes of being submerged in seawater, the surface of a marine facility is adhered to by macromolecules such as proteins, polysaccharides and glycoproteins, forming a base film.

Stage 2: Bacteria attach to the basement membrane and colonize it to form a biofilm. Since planktonic bacteria attach to the basement membrane through weak forces such as electrostatic interactions and van der Waals forces, this process is reversible at the beginning. However, bacterial adhesion becomes firm when the bacteria begin to secrete extracellular metabolites. This process can generally be completed within a few hours.

Stage 3: Since biofilm provides a favorable condition for small fouling organisms with multiple cells (e.g. diatom spores) to survive, their surfaces are covered by a mucus layer within a few days.

Stage 4: Mussels, moss worms, barnacles and algae and other large-scale fouling attached growth, this stage of the process can be completed in a month to two months, this stage is able to cover the surface of the material for several years.

However, these stages are not fixed, and there is no specific order between them. Coupled with the high level of complexity of marine ecosystems, the above theories can only be applied to a portion of the fouling organisms in marine ecosystems.

1.2.2 Development History of Anti-fouling Materials

According to the data records, in the period when human beings use wooden ships. People began to use asphalt, tar, arsenic compounds, lead plate, copper plate and so on as anti-fouling materials to cover the hull and other surfaces. In the iron ship, steel hulled ship appeared, metal cladding technology was gradually abandoned, due to the presence of copper will make the steel corrosion accelerate, however, people in the study of copper corrosion, found that the copper ion has a certain degree of fouling resistance, people began to apply the copper ion in the field of marine antifouling. To the middle of the nineteenth century, the use of a variety of toxic antifouling agents and natural resins for composite antifouling coatings was then the mainstream means of marine antifouling, antifouling agent of the main active ingredient of copper oxides, arsenic oxides, mercury oxides, etc., but due to the excessive harmfulness of heavy metals on the marine environment, so one after another was banned (Zhang, 2016; Chang, Chen, Chen, et al., 1996; Zhao, Zhang, Zhang, & Ding, 2017). In the middle of the twentieth century, people began to use organotin with high efficiency and broad-spectrum to replace copper compounds as antifouling poisons. In the 1970s, organotin self-polishing antifouling paints appeared and were widely used by people engaged in maritime activities (Liu, 2017). This kind of paint has good antifouling effect on the hull, can effectively reduce the hull resistance and thus minimize the fuel loss, but it is very harmful to the marine environment, people through the research found that organotin can be accumulated in fish, shells and plants for a long time, which will lead to genetic mutation of organisms, and the marine environment will be caused by the serious harm, so each country successively banned the use of organotin-related paint by the legislation. Therefore, various countries have legislated to ban the use of organic tin-related paints. In the late twentieth century, anti-fouling coatings with low toxicity have been researched and developed, among which cuprous oxide (Cu_2O) is the most important and widely used anti-fouling agent in anti-fouling coatings. Currently in the field of marine environment is the dominant coating based on cuprous oxide tin self-polishing anti-fouling coatings (TF-SPC), which mainly adopts a kind of rapid hydrolysis of the resin as the substrate, with low toxicity of cuprous oxide as an anti-fouling agent, the biggest advantage is that it does not contain will cause greater harm to the environment of marine organisms and toxicity of organotin, and at the same time, it can also effectively make the coating surface At the same time, it can effectively make the surface of the paint become smooth, so that it has the nature of self-polishing. Although the current Wuxi self-polishing anti-fouling coatings in the international marine anti-fouling coatings market has occupied a considerable degree of dominance, but the Wuxi self-polishing anti-fouling coatings are still common with some marine anticorrosion primer matching degree is not high in some cases, the mechanical adsorption and adhesion performance is relatively poor, as well as its saponified layer degradation need to rely fully on the seawater on the surface of anti-fouling coatings continue to wash

and other defects, there are some technical limitations. There are some technical limitations, which limit the application of Wuxi self-polishing antifouling coatings for marine activities (Yi, 2015).

- 1.3 Marine Antifouling Coatings
- 1.3.1 Self-polishing Anti-fouling Coatings

Self-polishing anti-fouling coating base material adopts a kind of polymer that can be hydrolyzed, through this copolymer in the seawater environment constantly and slowly hydrolyzed, the coating in the seawater environment through the hydrolysis/ion exchange interactions can be released from the metal ions and antifouling agent, and through the transfer of anti-fouling coatings attached to the surface of the marine organisms and the hydrolysis of the surface coatings in the seawater of the strong scouring and erosion of the detachment of the surface together, after many times of hydrolysis/abrasion process, a smooth surface can be formed, which can effectively achieve the effect of preventing the surface layer of the ship bottom from being passivated and marine organisms from adhering for a long period of time (Yu, Cong, Gui, Yu, Chen, & Wang, 2013).

The resin used in organotin self-polishing anti-fouling coatings (TBT-SPC) is usually a copolymerization of methacrylic acid, methyl acrylate and tributyltin methacrylate (TBTM). The paint can be hydrolyzed in seawater, releasing organotin toxins that are harmful to the marine environment, and gradually transforming into a water-soluble polyacrylate that separates from the underlying paint film to form a smooth surface. Organotin and its compounds on a variety of marine fouling organisms protection effect is very significant, from the 1960s in a variety of marine antifouling coatings have been widely used in a variety of marine antifouling coatings, the various species of marine organisms have a certain degree of antifouling effect, and antifouling life span of up to about 5 years (Liu, 2010). Organic tin self-polishing antifouling coatings appear in the development process of marine antifouling coatings has a very great significance, but its drawbacks are also fatal, it brings efficient anti-fouling effect at the same time will also be on the marine ecosystem to bring great damage, the World Maritime Organization banned the use of the antifouling coatings in 2008, tin self-polishing marine antifouling coatings are slowly beginning to replace tin self-polishing coatings.

Wuxi self-polishing anti-fouling coatings and tin self-polishing anti-fouling coatings, their resins are used in methacrylate copolymers, but Wuxi self-polishing anti-fouling coatings itself is the structure of the branched chain, is the use of copper, zinc, and silica elements instead of tin, the development of a side-chain hydrolyzed type of poly(acrylic acid) copper, poly(acrylic acid), poly(zinc acrylate), and poly(acrylic acid), silanes ester resins. Due to copper ions and zinc ions of the antifouling effect is far less than organic tin, and silane ester groups do not have the basic antifouling ability, so should add Cu₂O to be able to give its antifouling effect, to ensure that this tin self-polishing antifouling coatings antifouling broad-spectrum. Wuxi self-polishing antifouling paint antifouling principle and tin self-polishing antifouling paint principle is some similar places, the side base of the bivalent copper, zinc or silane ester group ion exchange or hydrolysis, through the ion exchange exudate ions to achieve antifouling effect, after hydrolysis of the resin acid salt in the seawater under the dissolution and

scrubbing effect of continuous shedding, to achieve the effect of self-polishing (Wang, 2014; Hu, 2012; Ye, Chen, Ma, Wu, & Zhang, 2017).

1.4 Low Surface Energy Antifouling Coating

Before the marine fouling organisms attach to the surface of the coating, first of all, through the secretion of a variety of mucus to infiltrate the surface, and then through a series of chemical action, electrostatic action, mechanical connection of one or more of these mechanisms to make the marine fouling organisms can be more firmly attached to the surface of the bottom of the ship to carry out marine activities. Low surface energy material has very low surface energy, it can not only effectively inhibit the infiltration of the liquid secreted by the fouling organisms, so that the dispersion of the surface of the material deteriorates, thus effectively preventing the attachment of the fouling organisms, even if the fouling organisms are attached to the surface, the fouling organisms attached to the surface have a very low adhesion force, and can be easily removed under the effect of the seawater washing and other external forces. The main advantage of low surface energy antifouling coatings is that they are not as toxic as tin self-polishing, and their effective service life is very long, which is of great technical and applied research value. It is generally believed that the surface energy of coatings is only lower than 25 mJ/m2, i.e., the contact angle between the surface of the coating and the liquid is more than 98° before it can have a good antifouling effect. The antifouling effect of low surface energy antifouling coatings is not only affected by the surface energy, but also related to the modulus of elasticity of the coating, the thickness of the coating, and the smoothness of the coating surface (Zhao, 2010; Coulson, Woodward, Badyal, et al., 2000).

Low surface energy marine antifouling coatings need to meet the following conditions in order to have good antifouling effect.

(1) Low modulus of elasticity: due to the low modulus of elasticity, the marine fouling organisms attached to the coating can be peeled off under small external force.

(2) Smooth surface: a relatively smooth surface allows the marine fouling organisms to be dislodged more easily.

(3) Appropriate thickness: to prevent the control of interfacial fracture.

Low surface energy antifouling coatings used in the low surface energy resin has a great influence on its antifouling effect. At present, the resin used for low surface energy antifouling coatings is mainly composed of silicone resin, fluorocarbon resin and fluorosilicone resin.

However, low surface energy silicone marine antifouling coatings still have the following problems.

(1) Poor adhesion to certain substrates, poor recoatability, and difficult construction treatment.

(2) The mechanical strength and stability of low surface energy coatings are poor. The surface of the coating is easily scratched by friction or broken for other reasons. Deliberate efforts to increase the mechanical stability of low surface energy antifouling coatings will result in a significant reduction in their fouling release properties.

(3) It is only suitable for high-speed ships traveling on the sea, and the anti-fouling performance of ships with relatively slow speed on the sea is not as good as that of high-speed ships, and the surface of the anti-fouling coating is easy to gather all kinds of diatomite, which is difficult to remove.

(4) When the added silicone oil is gradually lost to the point of disappearing, the silicone coating will rapidly become brittle or even cracked, and the marine fouling organisms will be attached to the surface of the coating very quickly, so much so that it greatly restricts its antifouling ability to the desired effect (Gui, 2008).

1.5 Research Status of Marine Antifouling Coatings

At present, the awareness of marine environmental protection is getting higher and higher, and the research trend of marine anti-fouling coatings at home and abroad is gradually developing towards the non-pollution of the marine environment and achieving the ideal anti-fouling effect. At the same time, the traditional anti-fouling coatings are also improved to get better results.

For the improvement of new self-polishing antifouling materials, we have good results, in a kind of anti-fouling materials containing grafting antifouling agent research, Ocean University of China, Yu Liangmin, etc. prepared a class of grafted organic acids and chorizol monomer of a functional zinc acrylate resin, the shallow sea hanging plate test shows that, in order to benzoic acid, p-toluic acid, m-toluic acid, cyclohexanic acid as an organic acid, hanging chorizol analogues of the structure of the monomer of functionality, the zinc acrylate resin has good performance. Zinc acrylate resin has good physical properties and anti-fouling properties (Zhang & Yu, 2010). The presence of active molecules on the surface of the coating is crucial for the antifouling effect. It depends on their diffusion in the film. (Fabienne, Isabelle, Jean, Val crie, & Karine, 2007).

In the field of low-surface-energy antifouling coatings, Shen (2017) prepared marine antifouling coatings with low-surface-energy fluorine- and silicone-modified resins, using the organofluorine monomer dodecafluoroheptyl methacrylate (FMA) and the organosilicone monomer γ -(methacryloyloxy)propyltrimethoxysilane (KH570) to modify acrylic resins; the synergistic effect of fluorine-silicone on the hydrophobicity of the coating film was significantly superior to that of fluorine-silicon monomers alone. The effect of fluorosilicon synergism on the hydrophobicity of the coating film was significantly better than that of fluorine and silicon alone, and the coating film obtained by synergistic action had lower surface energy. Zhou Feng's team prepared semi-interpenetrating polyvinyl alcohol polymer networks (SIPN) by integrating various charged components into polyvinyl alcohol polymers, and the contact angles were measured to be above 150°, which indicated that the polymers were able to effectively inhibit the adhesion of green algae and diatoms.

Finally, the research progress on biomimetic antifouling coatings is also a relatively more important research direction, the surface of various algae in the ocean can secrete and release some active substances to inhibit the adhesion of marine fouling organisms, and these naturally active substances can be used as antifouling agents after extraction and purification. In addition, capsaicin and piperine

extracted from terrestrial plants (e.g., chili peppers and peppercorns) can also be used to inhibit the adhesion of marine fouling organisms. However, the content of the above active substances in general plants is usually low, the extraction and purification steps are complicated, and the cost of large-scale preparation is high. The preparation of antifouling agents with a structure similar or superior to that of the natural active substances by chemical synthesis is a more efficient and suitable method of application.

However, bionic marine coatings cannot be used on a large scale due to the complexity and high cost of the preparation process.

1.6 Significance and Main Content of the Research

Nowadays, human activities in the ocean are becoming more and more frequent. The facilities and equipments used in marine activities need to be protected by antifouling coatings. The awareness of environmental protection has been emphasized by countries all over the world, and the corresponding laws and regulations have been gradually established and perfected. Anti-fouling materials that pollute and damage the marine ecological environment will be gradually eliminated, and at present, anti-fouling coatings that are friendly to the marine ecological environment are the main development direction of developing new anti-fouling materials for the oceans. China also attaches great importance to this, China is a fishing country since ancient times, the number of sea activities is a huge number, but because of China's anti-fouling coatings for the sea started a little later than other countries, in the non-toxic, friendly to the marine environment and other aspects of the research there is also a certain gap, so the development of the significance of the development of an efficient and non-polluting anti-fouling coatings for the economic development of China's marine economy has a very important significance. Therefore, the development of efficient and non-polluting marine antifouling coatings is of great significance for the economic development of China's ocean.

The main content of this paper is the use of single components or blends of biodegradable materials such as polycaprolactone (hereinafter referred to as PCL) and polylactic acid (hereinafter referred to as PLA) as the resin base. By adding a degradation enzyme or a hydrolysis promoter (polysaccharide additive) to the resin base material, the resin base material has a hydrolysis ability; by adding a bio-friendly antifouling agent, including but not limited to capsaicin (hereinafter hereinafter referred to as CPC), lactic acid, formic acid and the like, to the hydrolyzed base material, the coating has a fouling prevention ability. By adjusting the content of different components in the antifouling coatings were carried out, and the adhesion performance tests were conducted to obtain the antifouling coatings composition ratio intervals that could stabilize the film formation and have good adhesion ability. After that, we used the magnetic stirrer and other experimental equipments to simulate the method of hanging plate at sea to conduct experiments and make observation records, so as to obtain a solution of anti-fouling coating preparation for marine static aquaculture devices.

2. Experimental Section

2.1 Experimental Program

This experiment will be prepared by polycaprolactone (PCL)/polylactic acid (PLA), capsaicin (CPC), trichloromethane (hereinafter referred to as CHCL₃ in this paper), and starch after mixing and sufficiently dissolved as antifouling coatings on acrylic glass panels, to prepare an experimental sample of antifouling coatings on acrylic glass panels as a substrate, the experimental samples with and without starch were placed in a constant temperature magnetic stirrer, simulating the environment of tropical seawater, taken out every 24 hours, weighed and recorded using a hair dryer, and observed with an electron microscope on the surface. The experimental samples with and without starch were put into a constant-temperature magnetic stirrer to simulate the tropical seawater environment, and were taken out every 24 hours, weighed and recorded after 10 minutes of drying with a hair dryer, and the surface morphology was observed and photographed with an electronic magnifying glass.

In order to realize stable film formation and good adhesion of antifouling coatings, it is necessary to find out the composition ratio of raw materials for housing coatings and screen the ratio interval.

We used acrylic glass panels as the substrate surface with antifouling needs, divided it into 30mm×50mm size, and each group of antifouling coatings with the proportion of the antifouling coatings were coated on four experimental substrates to form a control experimental group. After 72 hours of natural air drying at room temperature in order to obtain the experimental samples.

2.2 Experimental Sample Numbers

2.2.1 Polycaprolactone (PCL)-based Antifouling Coating Sample Number

Sample number	Proportions (CHCL ₃ : PCL: CPC)
L1-1~L1-4	10:1:1
L2-1~L2-4	15:1:1
L3-1~L3-4	20:1:1
L4-1~L4-4	25:1:1
L5-1~L5-4	30:1:1
L6-1~L6-4	35:1:1
LS1-1~LS1-4	11:1:1
LS2-1~LS2-4	12:1:1
LS3-1~LS3-4	13:1:1
LS4-1~LS4-4	14:1:1
LS5-1~LS5-4	16:1:1

Table 1. PCL-based Unstarch A	ntifouling Coating S	Sample Numbers
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Sample number	Proportions (CHCL ₃ : PCL: CPC: Starch)
D1-1~D1-4	20:1:0.8:0.2
D2-1~D2-4	20:0.8:1:0.2

Table 2. PCL-based Plus Starch Antifouling Coating Sample Numbers

3. Results and Discussion

3.1 Polycaprolactone (PCL) Based Antifouling Coatings

Polycaprolactone (PCL), also known as $poly(\epsilon$ -caprolactone), has the appearance of a white solid powder, is non-toxic, insoluble in water, and easily soluble in a variety of polar organic solvents. PCL has good biocompatibility, good compatibility with organic polymers, and good biodegradability, and it can be completely decomposed into CO₂ and H₂O in soil and water environments within 6-12 months.Thus, it was chosen as one of the substrates for the present test (Yao, 2013).

In this experiment, the solvent method was adopted for the preparation, and the starch-free samples were first made by mixing PCL (solid), CHCL₃ (liquid), and PCP (solid) proportionally. Firstly, they were weighed separately, and then mixed at room temperature according to the ratio of CHCL₃:PCL:PCP at 10:1:1, 15:1:1, 20:1:1, 25:1:1, 30:1:1, and 35:1:1, respectively, and after the solutes were all dissolved, the solutes were uniformly coated on an acrylic glass plate with a brush, and then dried naturally at room temperature to determine the optimal ratio interval by observing its adherence, and the film-forming condition. Determine the optimal ratio interval. The following is a sample photo of each ratio.



Figure 1.1. PCL 10:1:1 Scale Sample



Figure 1.2. PCL 15:1:1 Scale Sample

As shown in Figure 1.1 for the composition ratio of 10:1:1 (CHCL₃:PCL:CPC), it can be seen that the paint mixed according to this ratio is more viscous, the thickness of the film varies, and can not form a smooth film, so it is deduced that the solvent ratio is too low, i.e., the proportion of the appropriate CHCL₃ should be higher.

As shown in Figure 1.2 for the photo of the sample with the composition ratio of 15:1:1 (CHCL₃:PCL:CPC), it can be seen that the paint mixed according to this ratio has a moderate viscosity, good adhesion effect, stable film formation, and the surface is relatively smooth, so it is deduced that the ratio before and after this ratio should be the appropriate ratio interval.



Figure 1.3. PCL 20:1:1 Scale Sample



Figure 1.4. PCL 25:1:1 Scale Sample

As shown in Figure 1.3, a photograph of a sample with a composition ratio of 20:1:1 (CHCL₃:PCL:CPC), it can be seen that the consistency of the paint mixed at this ratio is a little thinner than that of the 15:1:1 (CHCL₃:PCL:CPC) ratio, and the thickness is on the thin side as well. It remains to be seen how subsequent samples will turn out to be in order to determine the final appropriate ratio range.

As shown in Figure 1.4 for the composition ratio of 25:1:1 (CHCL₃:PCL:CPC) for brushing after the experimental samples macroscopic photographs, using 25:1:1 for mixing the experimental raw materials viscosity is low, for brushing can be smooth film formation, but its coating thickness uniformity is poorer, it is more difficult to meet the antifouling coatings uniform film formation requirements. Therefore, the composition ratio interval of antifouling coating with CHCL₃:PCL:CPC as raw material should be controlled between 10:1:1 (CHCL₃:PCL:CPC) and 20:1:1 (CHCL₃:PCL:CPC).



Figure 1.5. PCL 30:1:1 Scale Sample



Figure 1.6. PCL 35:1:1 Scale Sample

As shown in Figure 1.5 for the composition ratio of 30:1:1 (CHCL₃:PCL:CPC) of the sample photos, can be seen in accordance with this proportion of the mixing of the paint began to gradually become transparent, the thickness of the thinning, which can be seen to the ratio after the solvent proportion has begun to be high. It cannot be used as a suitable ratio.

As shown in Figure 1.6 for the composition ratio of 35:1:1 (CHCL₃:PCL:CPC) sample photos, can be seen in accordance with this ratio of mixed coatings compared to the previous ratio has been too thin, after mixing the solution is also becoming more and more transparent, the thickness of the film is also very thin, the film is difficult to form a film, the amount of solvent is already far greater than the amount of solute, so it can not be used as a suitable ratio.

By analyzing the surface morphology of antifouling coatings with different composition ratios, it was concluded that the suitable composition ratio interval was between 10:1:1 (CHCL₃:PCL:CPC) and 20:1:1 (CHCL₃:PCL:CPC), and in order to further determine the optimum composition ratios in the ratio interval, the ratios of 11:1:1, 12:1:1, 13:1:1, 14:1:1, 16 :1:1 as ratios for the preparation of experimental samples respectively.



Figure 1.7. PCL 11:1:1 Scale Sample



Figure 1.8. PCL 12:1:1 Scale Sample

As shown in Figure 1.7, the surface morphology of the antifouling coating sample with a composition ratio of 11:1:1 (CHCL₃:PCL:CPC) is shown in Figure 1.7. It can be seen through the surface of the antifouling coating that the effect of the coating mixed according to this ratio is similar to that of the sample with a composition ratio of 10:1:1 (CHCL₃:PCL:CPC), with a high degree of consistency, which does not result in the formation of an antifouling coating layer with a homogeneous thickness. . As shown in Figure 1.8, the surface morphology of the antifouling coating sample with a composition ratio of 12:1:1 (CHCL₃:PCL:CPC) is shown in Figure 1.8. It can be seen from the surface of the antifouling coating that the coating effect of the paint mixed according to this ratio is not much different from that of the sample with a composition ratio of 10:1:1 (CHCL₃:PCL:CPC) and 11:1:1 (CHCL₃:PCL:CPC), and the antifouling coating cannot form a uniform thickness layer. could not form an antifouling coating layer of uniform thickness.





Figure 1.9. PCL 13:1:1 Scale Sample

Figure 1.10. PCL 14:1:1 Scale Sample

As shown in Figure 1.9, the surface morphology of the antifouling coating sample with a composition ratio of 13:1:1 (CHCL₃:PCL:CPC) is shown in Figure 1.9. It can be seen through the surface of the antifouling coating that the coating effect of the paint mixed according to this ratio has been improved compared with that of the samples with the ratios of 10:1:1 (CHCL₃:PCL:CPC), 11:1:1 (CHCL₃:PCL:CPC), and 12:1:1 (CHCL₃:PCL:CPC). (CHCL₃:PCL:CPC) ratio samples have shown improvement in the surface smoothness after film formation.

As shown in Figure 1.10, the surface morphology of the antifouling coating sample with a composition ratio of 14:1:1 (CHCL₃:PCL:CPC) is shown. It can be seen through the surface of the antifouling coating that the paint application effect of the paint mixed according to this ratio is closer to that of the sample with a ratio of 15:1:1 (CHCL₃:PCL:CPC), but with a slightly higher degree of viscosity.



Figure 1.11. PCL 16:1:1 Ratio Samples

As shown in Figure 1.11, the surface morphology of the antifouling coating sample with a composition ratio of 16:1:1 (CHCL₃:PCL:CPC) is shown in Figure 1.11. It can be seen through the surface of the antifouling coating that the painting effect of the coatings mixed according to this ratio is also close to that of the sample with a composition ratio of 15:1:1 (CHCL₃:PCL:CPC), and the film-forming condition is good.

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In summary, the most suitable ratio interval for the antifouling coating prepared with PCL as the substrate should be between 10:1:1 and 20:1:1, which can form the experimental samples with good viscosity, relatively smooth surface, uniform thickness distribution and good adhesion.

3.2 Research on Hydrolysis Properties of Anti-fouling Coatings

Using the optimal ratio intervals previously obtained for the different materials, I added starch to a polycaprolactone-based antifouling coating with a ratio of 20:1:1 (CHCL₃:PCL:CPC), and a polylactic acid-based antifouling coating with a ratio of 25:1:1 (CHCL₃:PLA:CPC), respectively.

3.2.1 Polycaprolactone-based Antifouling Coatings with Added Starch

The experimental procedure was the same as the previous one, this experiment was also prepared by solvent method, where PCL, CHCL₃, CPC and starch were mixed proportionally. Firstly, tetrachloromethane liquid, polycaprolactone granules, capsaicin and starch were weighed separately. In order to standardize the amount of starch, I set the ratio of starch at 0.2, after which the liquid tetrachloromethane, polycaprolactone granules, capsaicin, and starch were mixed at room temperature in the ratios of 20:1:0.8:0.2 and 20:0.8:1:0.2, respectively, and the solutes were all dissolved, then uniformly coated on an acrylic glass plate with a brush and naturally air-dried at room temperature before being used to carry out the next step of the experiment. The following are photos of the samples in these two ratios.



Figure 1.12. PCL+starch 20:1:0.8:0.2 Ratio Sample



Figure 1.13. PCL+starch 20:0.8:1:0.2 Ratio Sample

3.3 Simulation of Seawater Hanging Plate Experiment

In order to investigate the effect of starch on the hydrolysis of antifouling coatings made using single components or blends of biodegradable materials such as polycaprolactone (PCL) as the resin base. I will conduct a set of comparative experiments in which samples of polycaprolactone-based antifouling coatings, LS3-1 without starch and D1-3 with starch, were placed in a seawater environment simulated by a magnetic stirrer, and were taken out every 24 hours and weighed and recorded after a 10-minute blowing with a hair dryer, and the surface phenomena were observed and photographed with a microscope every month.

The following data and photographs were taken during the 4-month experiment. Photograph of LS3-1 sample:



Figure 1.14. LS3-1

Figure 1.14 shows a photograph of sample LS3-1 initially, untested, with a clean surface and white paint color.



Figure 1.15. LS3-1 Microscopic Photograph

Figure 1.15 shows a photograph of sample LS3-1 in its initial state under a microscope, the surface is free of foreign matter and there are some black dots irregularly distributed on it.



Figure 1.16. LS3-1 (13)

Figure 1.16 is a photograph taken of sample LS3-1 placed in a magnetic stirrer for 13 days, where foreign matter began to appear, attached to the surface of the membrane. The peripheral parts of the membrane also gradually began to show attachments.



Figure 1.17. LS3-1(13) Microscope Shot

Figure 1.17 is a photograph taken under a microscope of sample LS3-1 placed in a magnetic stirrer for 13 days, and compared to the photograph at the beginning the surface is starting to show irregular lumpy stains with a few yellow stains.



Figure 1.18. LS3-1 (27)

Figure 1.18 is a photograph taken of sample LS3-1 placed in a magnetic stirrer for 27 days, with an increase in the amount of foreign matter on the surface and some areas of denser foreign matter.



Figure 1.19. LS3-1(27) Microscopic Photographs

Figure 1.19 is the sample LS3-1 placed in the magnetic stirrer 27 days under the microscope taken photos, it can be clearly seen that its surface compared to the previous compared to the phenomenon of localized dissolution, the original smooth surface of the coating, the appearance of grooves sagging, for the dissolution of the part of the presentation of the bun-type bulge.



Figure 1.20. LS3-1 (74)

Figure 1.20 is a photograph taken of sample LS3-1 placed in a magnetic stirrer for 74 days, where the surface of the membrane was almost completely covered with adhesions, while foreign material began to grow on the acrylic glass plate surrounding the membrane.



Figure 1.21. LS3-1(74) Microscopic Photographs

Figure 1.21 is a photograph of sample LS3-1 taken under a microscope when it was placed in a magnetic stirrer for 74 days, which shows that the furrowed subsidence and bun-type bumps on the surface have become more pronounced, and yellow stains are beginning to increase.



Figure 1.22. LS3-1 (100)

Figure 1.22 is a photograph taken of sample LS3-1 placed in a magnetic stirrer for 100 days. It can be seen that the foreign matter completely covers the surface of the membrane while its thickness is increasing, and at the same time the acrylic glass plate around the membrane is gradually covered by the foreign matter.



Figure 1.23. LS3-1(100) Microscope Shot

Figure 1.23 shows a photograph of sample LS3-1 taken under a microscope after 100 days in a magnetic stirrer, where it can be seen that the yellow stains deepen in color and cover a larger area.



Figure 1.24. Microscope Shots of the Four Stages of the LS3-1 Experiment

Figure 1.24 shows a comparison of the photographs of the four stages, it can be seen that the experimental sample LS3-1 prepared with polycaprolactone as the base material without starch, the surface of the surface with the advancement of the experimental time, the surface of the groove-like subsidence, for the dissolved part of the bun-type bulge, and the phenomenon is becoming more and more pronounced, at the same time, the color of the yellow stains gradually deepen.



Figure 1.25. Variation in Hydrolyzed Mass of Sample LS3-1

Figure 1.25 is a mass-time graph made from the results of the mass data recordings obtained after sample LS3-1 was removed from the magnetic stirrer daily and subjected to a 10-minute blast of cold air from a hair dryer. From the graph it can be seen that the weight of the sample is generally in an upward trend, with a large growth rate in the early part of the experiment, accompanied by the continuation of the experiment, there were several mass decreases in the middle of the experiment, but none of them lasted for a long period of time and fluctuated more frequently, but along with the experimental process, the trend of the growth of its weight became slower.

4. Conclusions and Outlook

4.1 Conclusion

In this paper, coatings of bionic antifouling materials based on polycaprolactone and polylactic acid were prepared by the solvent method, and the most suitable ratio interval was searched by varying the proportions of several experimental ingredients and observing the surface morphology and adhesion after film formation. Experimental samples of starch added to the original ingredients were prepared in time, and their weight data were recorded and photographs were taken to study the effect of added starch on the hydrolysis ability of the resin base material. The main research conclusions are as follows: (1) Antifouling coatings based on polycaprolactone (PCL), the solubility of PCL in CHCL₃ is better, and it can be dissolved in the case of low solvent percentage, easy to form a film, and the surface of the film after formation is smooth, and the thickness is relatively uniform.

(2) Starch was added to the experimental samples prepared with polycaprolactone (PCL)-based antifouling coatings, and the experimental samples without starch were simultaneously tested with magnetic stirrer and other experimental equipments to simulate the sea-hanging-board method, and observations were made to record that the change in the weight of the samples was a result of the

combined effects of the foreign matter attached to them, the adhering material, and the hydrolysis of the PCL. Through the pictures and experimental data, it was found that the weight of both samples showed an overall increasing trend, the sample with starch had higher water absorption, and gained weight a little faster in the early stage, but as the water absorption proceeded, the PCL began to undergo hydrolysis, and a significant decrease in weight gain was seen in the late stage of the experiment, whereas the weight gain of the sample with no starch added did not have a significant change in weight gain by the late stage of the experiment. Therefore, it can be shown that the addition of starch has a promotion effect on the hydrolysis ability of PCL, which is a kind of resin base material.

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