Preparation and performance of a low-cuprous oxide antifouling coating for static marine renewable energy facilities

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Abstract. Marine biofouling poses serious challenges to offshore structures and marine renewable energy facilities. Conventional self-polishing antifouling coatings typically rely on high cuprous oxide loadings and non-degradable polymer matrices, which limit static-condition performance and raise environmental concerns. Here, we report a low-cuprous-oxide (10 wt%) antifouling coating formulated with a degradable zinc acrylate resin (H100Z) as the primary film former. The H100Z resin combines main-chain degradation with side-chain hydrolysis to enable continuous surface renewal and controlled Cu^{2+} release. Combined with low-toxic biocides (DCOIT, CPT, ECONEA), the coating achieved smooth film formation, strong adhesion (~3 MPa), and stable performance after seawater immersion. The copper ion release stabilized at 8–10 $\mu g \cdot cm^{-2} \cdot d^{-1}$, indicating a steady self-polishing process. Field tests in Xiamen coastal waters demonstrated antifouling performance comparable to commercial coatings containing over 30 wt% Cu_2O, highlighting its potential for sustainable marine and renewable energy applications.

1. Introduction

Marine equipment and offshore engineering facilities have long faced the challenge of biofouling—the unwanted accumulation of marine organisms on submerged surfaces. Biofouling layers on platforms and structures can cause serious economic losses and safety hazards. For example, they increase hull frictional resistance and energy consumption, accelerate corrosion through acidic secretions, shorten service life, and raise maintenance costs [1]. Fouling can also destabilize floating platforms, clog pipelines and filters, and reduce water intake efficiency in critical facilities such as nuclear power plants. Among existing countermeasures, antifouling coatings remain the most practical and widely adopted solution.

Since 2008, tin-free self-polishing and fouling-release coatings have dominated industry development [2]. Modern self-polishing acrylic coatings replace organotin with copper, zinc, or silicon compounds and exploit hydrolyzable or ion-exchangeable side chains that erode under flow to release active agents. While effective for oceangoing vessels, these systems perform poorly under static or low-flow conditions because erosion depends on hydrodynamic shear [3]. In addition, most acrylic backbones are non-degradable and produce persistent exfoliated fragments (microplastics) after erosion [4-5]. Fouling-release coatings based on polysiloxanes or fluoropolymers reduce biocide use by providing low-energy, smooth surfaces, but often suffer from low mechanical strength, limited adhesion, and high cost, hindering broad application [6].

With the rapid development of marine renewable energy, such as floating offshore wind and wave energy systems, biofouling has become an even more critical issue. These moored and long-term submerged structures experience minimal water flow, rendering conventional antifouling coatings

ineffective [7]. In addition, existing coatings often contain toxic biocides and non-degradable resins [8]. Consequently, there is still no antifouling coating specifically designed for static marine renewable energy facilities that combines environmental compatibility, durability, and reliable antifouling performance.

The rapid expansion of marine renewable energy—notably floating offshore wind and wave energy—has increased demand for static antifouling solutions. These moored structures remain submerged for long periods with minimal water flow, where conventional ship coatings are ineffective. Moreover, environmental concerns over copper accumulation have prompted regulators to reassess allowable cuprous oxide contents [9]. Therefore, there is an urgent need for durable, environmentally compatible coatings specifically designed for static marine renewable energy infrastructure.

In this study, we employed a zinc acrylate resin (H100Z) that combines hydrolytic self-polishing with biodegradability as the primary film former to develop an environmentally friendly antifouling coating containing only 10 wt% Cu_2O. By coupling the resin's stable dual-degradation characteristics in slow-flowing seawater with the low-toxic antifouling agent design, the coating achieves a controlled self-renewal process and sustained antifouling performance under static marine conditions.

2. Experiment

2.1 Reagents and instruments

The main-chain degradable self-polishing zinc acrylate resin (H100Z, Shenzhen Haiwei New Material Technology Co., Ltd.). Rosin (analytical grade) was supplied by Jiangxi Huajin New Materials Co., Ltd.. Zinc oxide (≥99%) was purchased from Shandong Xingyuan Zinc Industry Technology Co., Ltd., and red iron oxide was obtained from Shanghai Shenhong Pigment Co., Ltd.. Talc powder and sepiolite powder were supplied by Lingshou Fengxin Mineral Powder Processing Factory. Polyamide wax was purchased from Clariant Co., Ltd.. Copper pyrithione (CPT) was obtained from Wuhan Rongcan Biotechnology Co., Ltd., while Econea [2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoro methyl-pyrrole] and SeaNine-211 [4, 5-dichloro-2-n-octyl-4-isothiazolin-3-one] were purchased from Wuxi Yaodexin Chemical Products Co., Ltd.. The dispersant BYK-9076 and the leveling-defoaming agent BYK-354 were supplied by BYK-Chemie GmbH. All other organic solvents were of analytical grade and obtained from Aladdin Reagent Co., Ltd.. A commercially available antifouling paint from an international coating brand was used as the control sample.

Instrument: The high-speed disperser sand mill stirring (Biuged, China), DZF 6210 Vacuum Drying Oven (Biuged, China), QTY-32 paint film bending tester (LeTkingok, China), BGD 186 intelligent Stormer viscometer (Biuged, China). BGD304 impacting testing machine (Biuged, China), BGD-500 digital tensile adhesion tester (Biuged, China), electronic thickness meter (Elcometer 456, Britain). BGD 296 specific gravity cup (Biuged, China).

2.2 Coating preparation

The H100Z resin, rosin, polyamide wax (as a thixotropic agent), dispersant BYK-9076, defoamer BYK-354, and butyl acetate were first placed in a mixing vessel and stirred at 1000 rpm for 20 min. While maintaining the same stirring speed, pigments and fillers, including red iron oxide, sepiolite powder, and talc powder, were successively added, followed by antifouling agents such as cuprous oxide (10 wt%), zinc oxide, CPT, DCOIT, and Econea. After the mixture was uniformly dispersed, grinding media were introduced, and the slurry was transferred to a sand mill for 2 h of grinding, ensuring a fineness of ≤50 μm. Subsequently, the controlled-release microcapsules containing antifouling agents were added to the coating and thoroughly mixed to obtain the static antifouling formulation. The final antifouling coating was then filtered through a 200-mesh screen.

2.3 Coating characterization

The color and surface appearance of the coated panels were visually examined under diffused natural daylight to evaluate uniformity and gloss. Viscosity was determined according to GB/T 2794, flash point according to GB/T 5208, density following GB/T 6750, and the volume solids content in accordance

with GB/T 9272. The drying time was measured according to GB/T 1728-1979, using Method B for surface drying and Method A for through drying, as specified in the standard. The antifouling performance of the coatings was evaluated through a shallow-sea immersion test conducted at the Dali Puyu Marine Test Station in Xiamen, China. Test panels coated with the experimental antifouling coatings were vertically mounted on a test frame in accordance with GB/T 5370-2007. The copper ion release rate of the coating was measured in accordance with GB/T 6824-2008.

The coating was applied in a sequence of three stages. First, a corrosion-resistant flake primer was air-sprayed in two layers, each with a dry film thickness of 150 μm, ensuring strong adhesion and substrate protection. An intermediate tie-coat (60 μm) was then applied to improve intercoat adhesion. Finally, two layers of static antifouling paint were sprayed, yielding a total dry film thickness of 240 μm. The coating exhibited good workability, forming a uniform surface without defects such as sagging or pinholes, and met all performance requirements upon inspection.

3. Results and discussion

3.1 Dual-degradation antifouling resin

In recent years, Professor Guangzhao Zhang's research group at South China University of Technology has integrated self-polishing and biodegradable technologies to develop a novel polymer featuring dual degradation mechanisms—main-chain degradation and side-chain hydrolysis [5]. The ester bonds in the polymer backbone can be readily cleaved by seawater or marine enzymes, generating small water-soluble fragments that promote continuous surface renewal. Meanwhile, hydrolyzable side groups gradually convert the polymer from hydrophobic to hydrophilic, enhancing solubility and accelerating surface erosion and antifouling efficiency (Figure 1). Through the synergistic action of these two pathways, the self-renewing antifouling surface achieves improved sustainability, controllability, and long-term resistance to marine biofouling. In this study, a main-chain degradable zinc acrylate self-polishing resin, developed based on Professor Zhang's research, was used as the primary film-forming material.

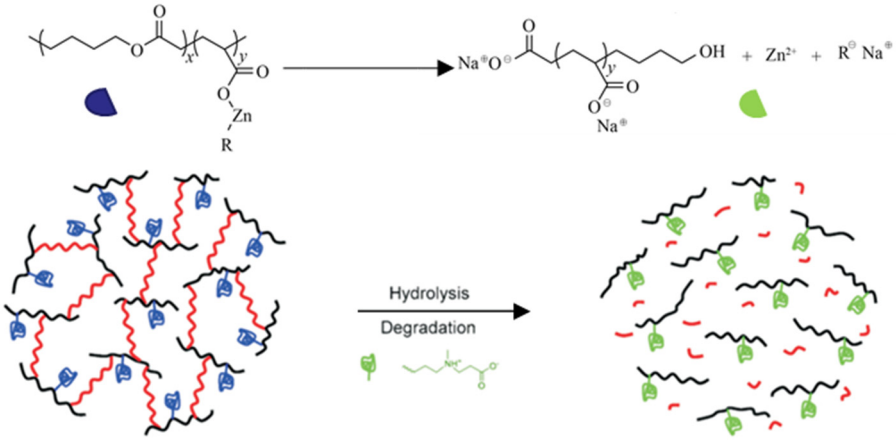

Figure 1. Schematic illustration of the main-chain degradation and side-chain hydrolysis of the H100Z resin [5].

3.2 Physical and mechanical properties of coatings

As shown in Table 1, the coating presented as a red viscous liquid with a solid content of approximately 80%, and its fineness met the required specifications. For antifouling coatings, adhesion, flexibility, and seawater immersion resistance are key performance indicators determining long-term durability. Adhesion reflects the coating's ability to form a strong interfacial bond with the substrate, directly affecting its stability under variable environmental conditions. Flexibility ensures coating integrity and performance under mechanical stresses such as bending, vibration, and impact. Moreover, because antifouling coatings are continuously exposed to seawater, excellent stability and resistance to degradation are essential.

Table 1. Physical and mechanical properties of low-cuprous oxide antifouling paint and coating.

Entry	Test standard	Results
Rotational viscosity (Pa·s)	ASTM D2196-2020	5.06
Non-volatile content (%)	GB/T 1725-2007	79.1
Impact resistant (cm)	GB/T 1732-2020	50
Color and appearance	/	Red, normal
Adhesion strength (MPa)	GB/T 5210-2006	3 (2.1~3.9), 100% C
Adhesion strength (MPa) after 30 days of artificial seawater immersion test	GB/T 5210-2006	2.55, 100% C
Adhesion strength (MPa) after 9-month shallow-sea immersion	GB/T 5210-2006 GB/T 5370-2007	2.39,100%C
Surface drying time, h Hard drying time, h	GB/T 1728-2020	1 24
Flexibility, mm	GB/T 1731-2020	1
Density, g/mL	GB/T 6750-2007	1.687
Fineness, μm	GB/T 1724-2019	55

The H100Z resin, characterized by a relatively low glass transition temperature and moderate molecular weight, combined with the appropriate addition of rosin, imparted exceptional flexibility to the coating film. The prepared coating exhibited an impact resistance of 50 cm and a flexibility rating of 1 mm—both meeting the highest grades specified in the relevant standards. Its adhesion strength reached 3 MPa, surpassing that of most commercial antifouling coatings. Even after 30 days of immersion in artificial seawater, the adhesion strength remained at 2.55 MPa, and the film surface stayed smooth and defect-free. After nine months of immersion in shallow seawater, the coating maintained an adhesion strength of 2.39 MPa, comparable to that of the commercial control coating. These results confirm that the developed coating possesses excellent mechanical robustness, strong substrate adhesion, and superior durability under marine conditions.

3.3 Shallow-sea immersion test

To evaluate the antifouling performance of the low-cuprous-oxide coating, comparative tests were performed against a commercially available antifouling coating from an international manufacturer. The experiments were conducted in the coastal waters near Dali Pu Islet, Xiamen Island—a subtropical region characterized by a warm, humid climate and diverse fouling communities, mainly barnacles, bryozoans, and marine sludge with strong adhesion. Compared with other areas of the South China Sea, the Xiamen coastal waters experience more severe biofouling due to pollution and human activity. Therefore, this site provides a rigorous and representative natural environment for antifouling performance assessment.

As shown in Figure 2, after three months of exposure, both coatings exhibited smooth, intact surfaces with minimal organism attachment, indicating excellent short-term antifouling performance. After six months, the commercial control coating showed significant accumulation of marine sludge and mature barnacles, revealing poor static antifouling capability. In contrast, the low-cuprous-oxide coating remained largely free of barnacles and other fouling organisms, except for minor growth near the panel edges (organisms within 2 cm of the edge were excluded according to the evaluation standard). Excluding this edge effect, the low-cuprous-oxide coating displayed markedly superior antifouling performance.

After nine months, barnacle counts on both coatings decreased noticeably. Most barnacles near the edges of the low-cuprous-oxide coating had detached, leaving only a few small ones in the central area. In comparison, the surface of the control coating was almost entirely covered by marine sludge, while most barnacles originally attached to its central region had also detached, resulting in a barnacle count similar to that of the self-developed coating. Overall, the low-cuprous-oxide coating demonstrated antifouling performance comparable to international commercial coatings, despite containing only 10 wt% cuprous oxide—far below the typical 30–40 wt% used in industry. The excellent static antifouling

performance of the self-developed coating can be attributed to its dual-degradation characteristics, which enable effective surface self-renewal even under static seawater conditions, continuously exposing fresh surfaces that facilitate the steady release of environmentally friendly biocides [2].

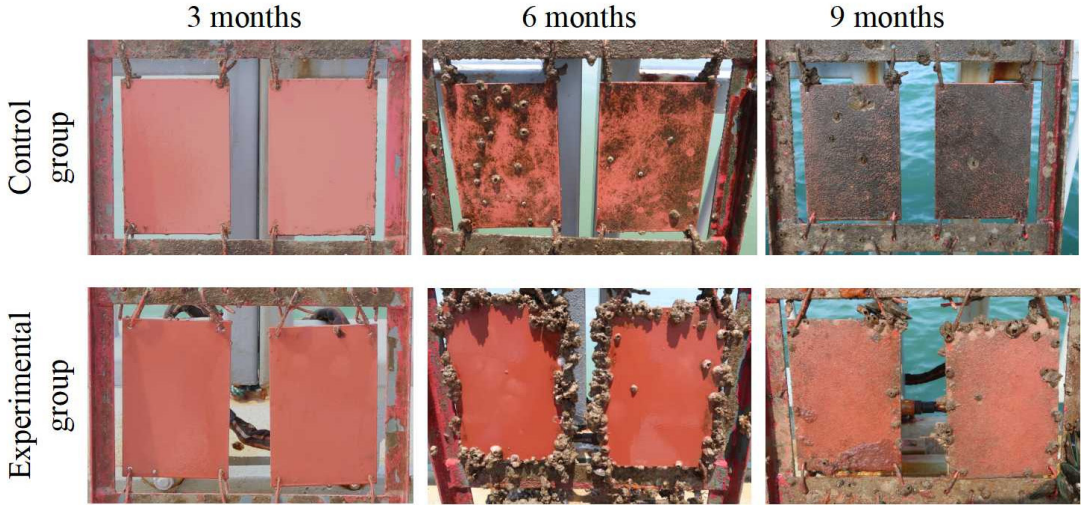

Figure 2. Digital photographs of antifouling coating panels from the experimental and control groups after 3, 6, and 9 months of shallow-sea immersion.

3.4 Copper ion release test

In accordance with domestic and international environmental protection regulations, antifouling agents with strong environmental toxicity—such as organotin compounds, DDT, and compounds containing lead, mercury, or arsenic—have been strictly prohibited. Therefore, all antifouling agents used in this study were environmentally degradable and exhibited low bioaccumulation potential. Among them, cuprous oxide (Cu_2O) provides excellent antifouling efficacy against hard-shelled marine organisms, although the released copper ions in seawater exhibit relatively high toxicity [10]. Investigating copper ion release behavior is thus crucial for understanding the coating's antifouling performance and underlying mechanism.

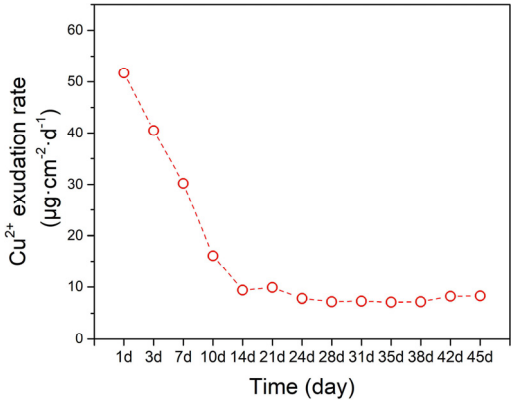

Figure 3. Copper ion release rate of the low-Cu_2O antifouling coating.

As shown in Figure 3, the developed coating exhibited an initially high copper ion release rate of up to 53 $\mu g \cdot cm^{-2} \cdot d^{-1}$ during early seawater immersion. With extended exposure, the release rate stabilized after day 14 and remained within 8–10 $\mu g \cdot cm^{-2} \cdot d^{-1}$ over the following month. This stable behavior can be attributed to the dual-degradation mechanism of the H100Z resin, which enables a continuous and controllable self-polishing process under static seawater conditions. The sustained surface renewal not only generates a dynamic interface unfavorable to biofouling attachment but also continuously exposes fresh, active Cu_2O, thereby ensuring a steady release of copper ions.

4. Conclusion

In conclusion, a low-cuprous-oxide antifouling coating was developed using the H100Z resin, which features both main-chain degradability and side-chain hydrolysis as the primary film-forming component. The formulation incorporated low-toxic biocides such as DCOIT, CPT, and ECONEA, together with a significantly reduced cuprous oxide content of only 10 wt%, far lower than that used in most commercial antifouling coatings. The prepared coating exhibited excellent application performance, forming a smooth and uniform film after air spraying. It also demonstrated outstanding flexibility and adhesion; after one month of immersion in artificial seawater, the adhesion strength remained around 2.55 MPa, indicating good stability. In shallow-sea exposure tests conducted in the coastal waters of Xiamen, the developed coating showed antifouling performance comparable to that of commercial self-polishing coatings from leading international brands, despite its much lower cuprous oxide content (typically above 30 wt%). Owing to its environmentally benign material design and excellent static antifouling performance, this coating holds significant potential for application in the rapidly growing field of marine renewable energy infrastructure.

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