

Synthesis and Use of a Perfluorinated Coumarin-Based Surfactant as an Antifouling Coating

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ABSTRACT

This study presents the design and evaluation of a novel hybrid surfactant based on perfluorocoumarin, developed for antifouling marine coatings. The surfactant was synthesized via the functionalization of coumarin with fluorinated chains and incorporated into a polymer matrix. Structural characterization by FTIR confirmed the successful integration of coumarin into the polymer through the reduction of O–H signals and the presence of characteristic C=O and C–F bands. UV-Vis analysis revealed a strong absorption peak at 281 nm, consistent with the $\pi \rightarrow \pi^*$ transitions of the coumarin core. Comparative antifouling tests demonstrated the limited performance of commercial paint (Micron Extra EU), which showed surface degradation and microbial colonization over time. In contrast, coatings formulated with the perfluorocoumarin surfactant exhibited excellent resistance to biofouling, surface integrity, and anti-corrosion performance. The hybrid system also showed anti-graffiti behavior and mechanical robustness. These findings highlight the potential of this eco-friendly surfactant for advanced marine applications, though further studies on long-term durability are recommended.

Keywords: Antifouling Coatings, Waterborne Polyurethane (WPU), Marine Biofouling, thermal Properties, antibacterial properties.

INTRODUCTION

The use of marine paints with high durability, extensibility, and notable antifouling properties is widespread. However, a critical issue often goes unnoticed to the naked eye [1].

Microscopic analyses have revealed that marine organisms can spontaneously adhere to submerged surfaces, forming invisible biofilms [2]. This biofouling process is particularly rapid in nutrient-rich and well-illuminated aquatic environments. The accumulation of such biological layers poses serious threats to biodiversity and the balance of marine ecosystems [3–5]. Degradation of paint films releases particulate matter, which can serve as a nutrient source for microorganisms. Over time, these organisms can evolve into larger macrofouling species with diverse morphologies [6]. To address this challenge, recent research has explored antifouling materials reinforced with nanoscale additives, such as nanocrystals [7]. While these materials show enhanced performance, a major drawback lies in the disruption of intermolecular interactions within the polymer matrix [8–10]. This destabilization leads to mechanical failure of the coating, manifested as film delamination and blistering (Fig.1), thereby accelerating degradation.

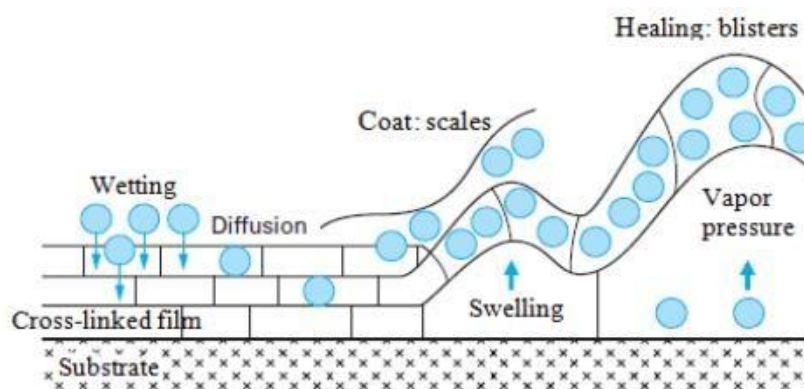


Fig. 1: Mechanically induced lifting of the paint film, where the coating detaches from the substrate and forms blister-like structures that accelerate the degradation process [11]

Advanced techniques, such as nuclear magnetic resonance (NMR) spectroscopy, have confirmed this degradation mechanism at the molecular level [12]. Several alternative approaches have been proposed, including polyester-based coatings (used in icebreaker hulls), non-biocidal mechanically cleanable paints, and fluoropolymer-based formulations [13–16]. Among them, fluoropolymers stand out for their outstanding chemical resistance, environmental stability, and long-lasting antifouling efficiency [17].

Polyurethane-based antimicrobial coatings have also shown potential, particularly due to their low surface energy and integration of bactericidal agents [18–21]. However, the presence of hydrophilic $-\text{CH}_2\text{OH}$ moieties within their structure compromises water resistance and limits long-term performance.

To overcome these limitations, we have undertaken both theoretical and experimental studies in our laboratory. We report here the synthesis of a novel perfluorinated surfactant functionalized with a coumarin moiety. This hybrid molecule exhibits excellent water repellency, weather resistance, and improved mechanical integrity [22–24], marking a significant step toward the development of durable and eco-friendly antifouling materials.

Perfluorinated surfactants, due to their low surface energy and chemical inertness, are ideal candidates for reducing environmental toxicity, minimizing degradation, and limiting the release of harmful substances into marine environments [25–27]. The compound synthesized in this study features a unique spiral molecular structure (Fig. 2), attributed to intramolecular hydrogen bonding [28, 29]. This architecture contributes to its superior performance compared to conventional coatings [30, 31], offering multiple advantages such as biocompatibility, non-toxicity, ease of processing, cost-effectiveness, and broad-spectrum antifouling efficiency [32–36].

In light of these promising characteristics, the objective of this study is to develop and evaluate this novel coumarin-functionalized perfluorinated surfactant as an effective and sustainable antifouling agent. Through comparative analysis with a commercial reference (Micron Extra EU), we aim to assess its structural integrity, thermal behavior, and antifouling performance, thereby demonstrating its potential for marine coating applications.

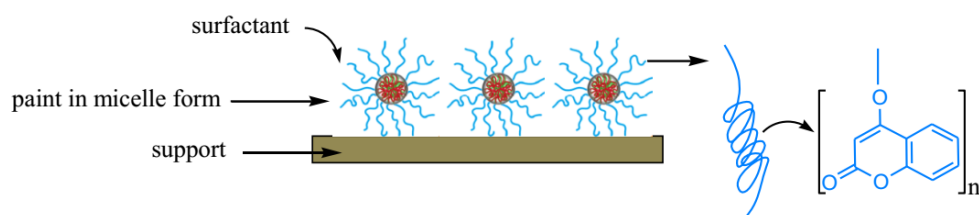


Fig. 2: Schematic representation of the surfactant on a support fixing the surfactant on the metal support [11]

EXPERIMENTAL PART

MATERIALS

1-Methoxypropan-2-ol and methanol (technical grade) were purchased from Macklin. Dimethylformamide (DMF) was obtained from the FILAB laboratory, and deionized water (H₂O) was prepared in-house. 4-Hydroxycoumarin (4-hydroxy-1-benzopyran-2-one, C₉H₆O₃) was supplied by Sigma-Aldrich. The initial perfluorinated compound was synthesized at the Montpellier Chemistry Laboratory (ENSCM), France.

In addition, the commercial antifouling product Micron Extra EU was purchased from a local distributor in Oran, Algeria.

PREPARATION OF THE PERFLUORINATED SURFACTANT

The initial product was synthesized under UV irradiation [37] in a solvent-free environment. Its structure was confirmed by proton nuclear magnetic resonance (¹H NMR) spectroscopy.

SYNTHESIS OF THE COUMARIN SURFACTANT

For the preparation of the final product, a stock solution was prepared by dissolving 4-hydroxycoumarin in dimethylformamide (C₃H₇NO) in a glass vial. The initial product (see Section **Preparation of the perfluorinated surfactant**), previously dissolved in water, was then added dropwise to this solution. The resulting mixture was stirred continuously at ambient temperature for 3 hours, as illustrated in Fig.3.

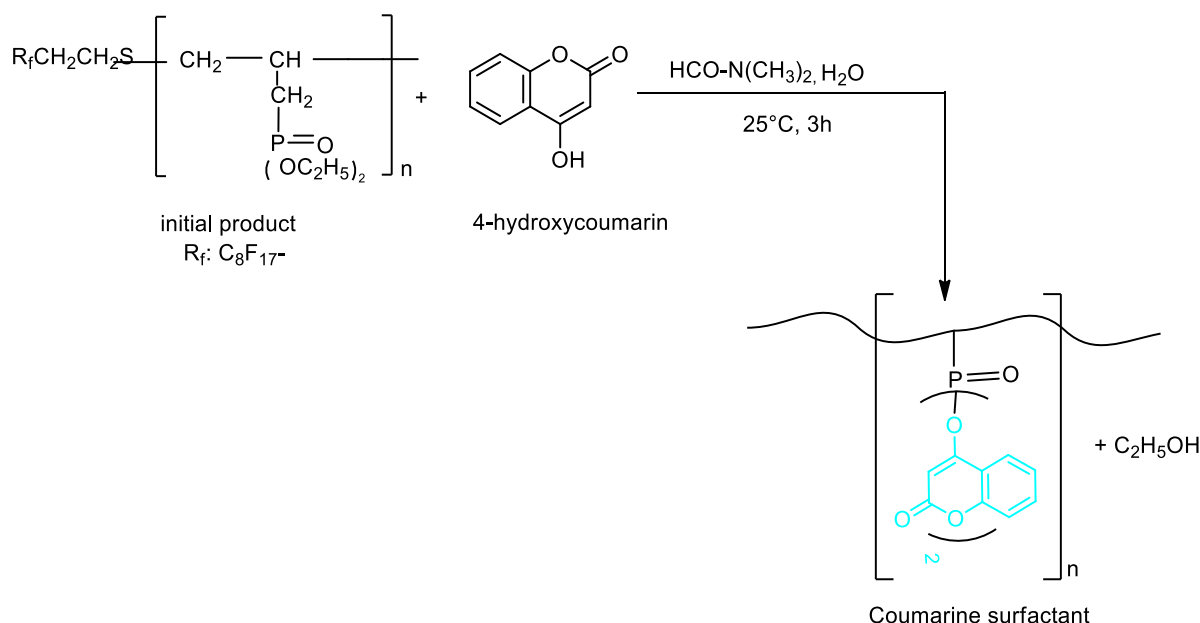


Fig. 3: Synthesis of the perfluorocoumarin surfactant. Formation of the final product during the synthesis process is illustrated

PREPARATION OF THE PLATES

Rectangular aluminum plates (7.5 cm × 6.5 cm, 3 mm thick) were used as substrates for the antifouling experiments. Prior to coating, the surfaces of the plates were sanded to enhance paint adhesion. Subsequently, the plates were cleaned with methanol to eliminate any residual contaminants (Fig.4).

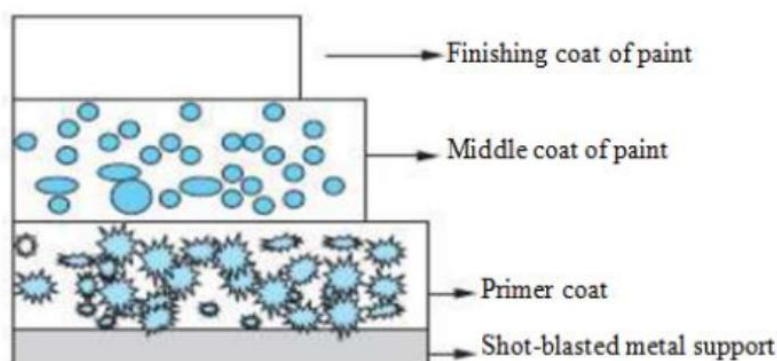


Fig. 4: General diagram illustrating the principle of protecting a metal immersed in seawater [38]

The paints are prepared by dissolving the resin in 2-methoxypropanol. The formulations are prepared in a laboratory DI-SPERME dissolver.

Each plate is painted on both sides in three successive coats (Fig.4), leaving at least 24 hours between applications. The application temperature is 20°C because below 15°C the paint dries too slowly and above 25°C it dries too quickly and does not adhere properly to the substrate.

The plates were left to dry for a week before being mounted on a metal support and then immersed in seawater [39].

CHARACTERIZATION

NUCLEAR MAGNETIC RESONANCE (NMR)

The ^1H nuclear magnetic resonance (NMR) spectra were recorded using a Varian UNITY INOVA 500 MHz spectrometer, with DMSO- d_6 as the solvent and tetramethylsilane (TMS) as the external standard. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The operating principle of this device is based on measuring the energy required to maintain a near-zero temperature difference between the sample (i.e., the substance under analysis) and an inert reference material. Both the sample and the reference are subjected to identical thermal conditions within a controlled heating/cooling environment, with the temperature program regulated by computer software (Pyris version 4.00).

The analysis was conducted under a nitrogen (N_2) atmosphere. Prior to sample introduction, the following parameters were set: a constant heating rate of 10 °C.min⁻¹, and a sample mass of 13 mg placed in a hermetically sealed aluminum crucible (according to instrument specifications). The samples were then loaded into the Differential Scanning Calorimetry (DSC) apparatus, and the temperature range was set from 50 °C to 450 °C. An isothermal hold of 15 minutes was applied at a temperature above the melting point (T_m) but below the decomposition temperature, to ensure complete melting and the destruction of any crystalline lamellae. Finally, the samples were cooled at a constant rate of 10 °C.min⁻¹ down to room temperature. This technique is frequently employed to determine glass transition temperatures (T_g), melting temperatures (T_f), as well as to measure fusion enthalpies and study the crystallization kinetics of polymeric materials.

RESULT AND DISCUSSION

STRUCTURAL CHARACTERIZATION BY FTIR

The chemical structure of the synthesized poly(propylene-coumarin) was investigated using Fourier Transform Infrared (FTIR) spectroscopy. The FTIR spectrum (Fig.5) displays a broad band around 3400–3200 cm^{-1} corresponding to O–H stretching vibrations. The marked reduction in intensity in this region, compared to that of unreacted coumarin, indicates the progressive disappearance of hydroxyl groups during the polymerization process. Distinct absorption bands observed at 2945, 2653, and 2536 cm^{-1} are characteristic of C–H stretching vibrations in aliphatic chains, confirming the presence of the propylene backbone. A strong band at 1675 cm^{-1} is assigned to C=O stretching of the coumarin lactone ring, while peaks at 1600 and 1452 cm^{-1} are attributed to aromatic C=C stretching. Furthermore, the presence of bands near 1263 and 1123 cm^{-1} suggests the formation of C–O–C and C–O linkages. Out-of-plane bending vibrations of aromatic C–H groups appear at 973, 839, and 750 cm^{-1} , confirming the retention of the coumarin moiety within the polymer matrix.

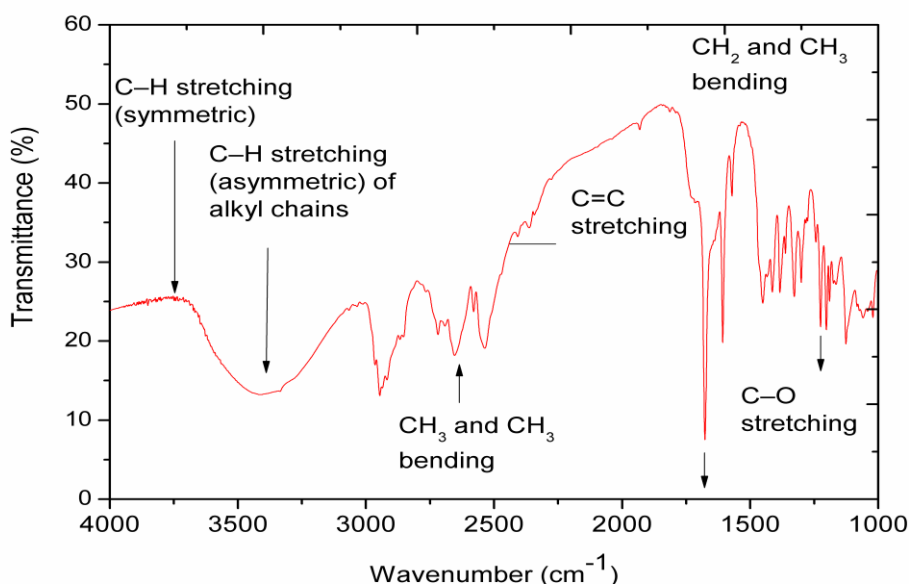


Fig. 5: FTIR spectrum of poly(propylene-coumarin)

DETERMINATION OF MAXIMUM ABSORPTION WAVELENGTH (UV-VIS)

UV-Visible spectroscopy was performed to determine the maximum absorption wavelength (λ_{max}) of the synthesized perfluorocoumarin surfactant. The UV spectrum (Fig.6) shows a strong absorption band centered at 281 nm, which is attributed to $\pi \rightarrow \pi^*$ electronic transitions within the conjugated aromatic system of the coumarin moiety. This prominent absorption confirms the preservation of the coumarin chromophore after fluorination. The intensity of the peak also indicates good solubility and stability of the surfactant in the solvent medium (likely ethanol or another polar organic solvent). These spectral features are consistent with the expected optical properties of fluorinated coumarin derivatives, supporting the successful synthesis of the hybrid surfactant.

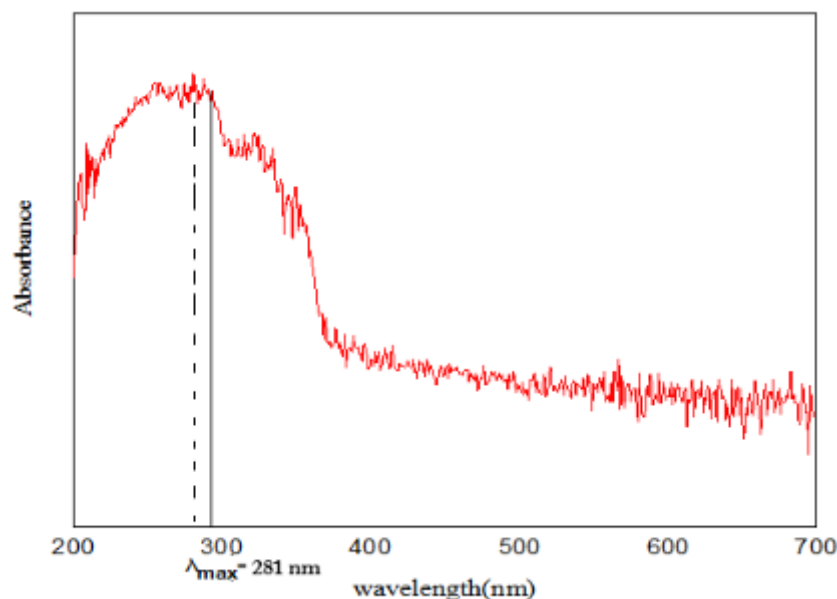


Fig. 6: UV-Visible absorption spectrum of the perfluorocoumarin surfactant

STRUCTURAL CHARACTERIZATION OF PERFLUOROCOUMARIN COATING

The ^1H NMR spectrum of the perfluorinated surfactant (initial product) showed the following signals: a triplet at 1.13 ppm and a split quartet at 4.10 ppm, attributed to the ethyl groups of the phosphonic moiety. A multiplet between 2.5–2.2 ppm was assigned to the CH_2 groups in the α -position relative to the C_8F_{17} chain and the β -position relative to sulfur. Another multiplet, observed in the 3.0–2.5 ppm range, was attributed to the CH_2 groups in the α -position on both sides of the sulfur atom. Signals in the 1.8–1.9 ppm region were ascribed to CH_2 groups in the γ -position relative to sulfur and the α -position relative to the phosphorus atom. Yield: 90% [40].

The ^1H NMR spectrum of the final perfluorocoumarin surfactant exhibited aromatic proton signals from the coumarin moiety between 7.0–7.2 ppm and a distinct signal at 8.2 ppm. (Fig.7) A peak at 12 ppm was assigned to the carboxylic acid proton, indicating partial hydrolysis. Yield: 75%.

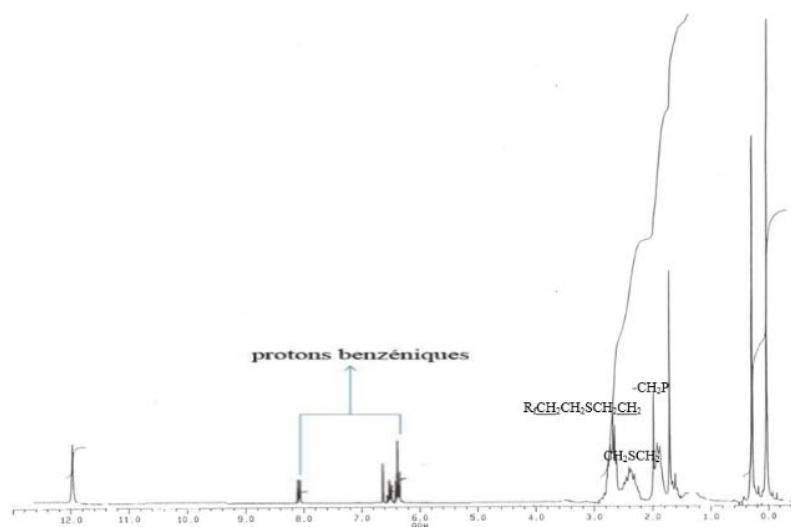


Fig. 7: ^1H NMR spectrum (200 MHz) of the final product (perfluorocoumarin surfactant)

THERMAL DSC PROPERTIES

Fluorinated surfactants such as perfluorocoumarin are attracting growing interest due to their unique properties, including chemical and thermal stability, low surface tension, and compatibility with various media [41, 42]. The thermal characterisation of these compounds is essential for evaluating their behaviour under processing or usage conditions, particularly in the fields of coatings, pharmaceuticals, and advanced materials.

Differential scanning calorimetry (DSC) can be used to detect and quantify thermal transitions such as melting, glass transition, crystallisation, and thermal degradation. This study aims to determine the main thermal transitions of perfluorocoumarin in a temperature range from 50 °C to 450 °C [41, 42].

The DSC curve obtained shows several characteristic peaks, indicating the main stages of thermal transition of perfluorocoumarin. [43] (Fig.8).

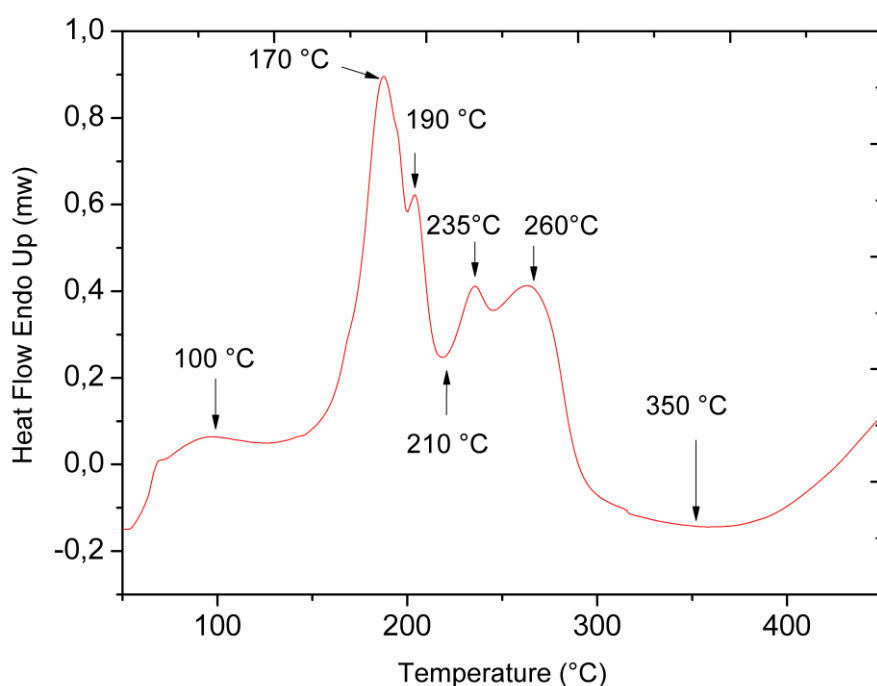


Fig. 8: DSC thermogram of the perfluorocoumarin-based surfactant showing multiple thermal events corresponding to moisture loss, molecular transitions, and thermal degradation

DSC analysis of perfluorocoumarin indicates good thermal stability up to approximately 350 °C, which is an advantage for thermally demanding applications Fig.8. The well-defined melting point at 170 °C indicates a well-organised structure, while subsequent transitions reflect either reorganisation phenomena or the onset of degradation (see the table below).

These results confirm that perfluorocoumarin is a thermally robust surfactant, suitable for industrial processes or formulations exposed to moderate to high temperatures [44].

Temperature (°C)	Transition type	Interpretation
~100 °C	Small endothermic peak	Loss of moisture or low Tg onset [45]
~170 °C	Intense endothermic peak	Main melting point (T _m)
~190 °C	Rapid thermal transition	Amorphisation Or post-merger restructuring
210–260 °C	Secondary endothermic peaks	Secondary transitions ou impurities
~350 °C	Wide endothermic transition	Start of thermal degradation

APPLICATIONS OF ANTIFOULING PAINT

The physical processes involved in the application of this antifouling paint are schematically illustrated in Fig.9 and 10.

The paint used in Fig. 9 is Micron Extra EU, a self-polishing antifouling coating designed to provide up to two years of protection with a single application, regardless of the level of biofouling, as specified by the manufacturer.

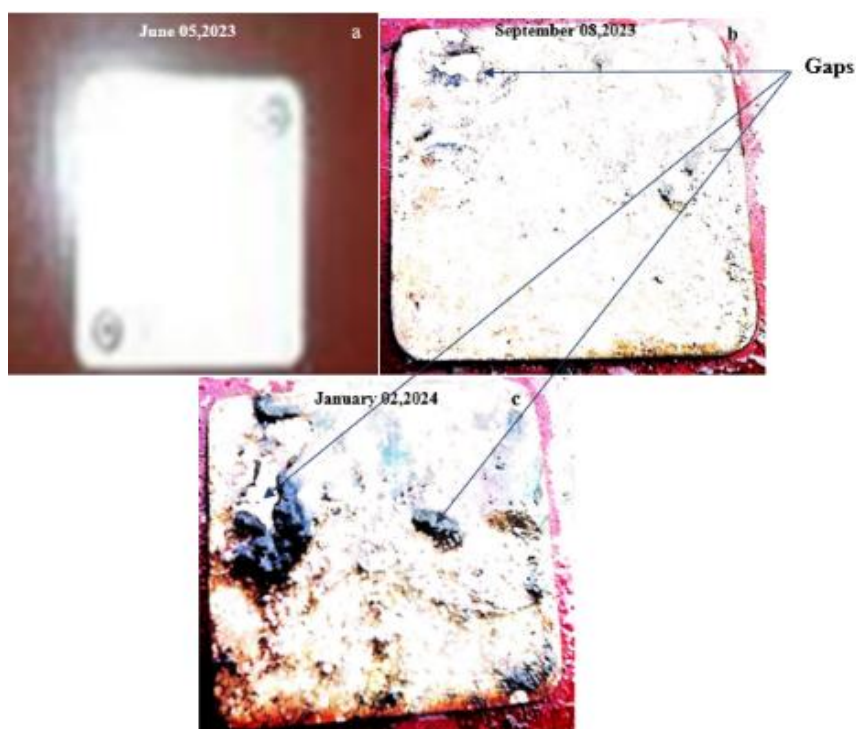


Fig. 9: Photographs of the coated plates following the application of the antifouling paint. Microbial colonization was visually monitored over the period from June 2023 to January 2024 [40]

In June 2023, no signs of fouling were detected, and the coated plate (Fig.9a) effectively prevented colonization by macrofouling organisms. However, by September 2023, initial microbial colonization was observed in localized areas, particularly within micro-gaps formed as a result of paint swelling and partial degradation (Fig.9b) [46].

Fig.10 further illustrates the progression of this swelling process, which accelerates over time and contributes to the formation of structural discontinuities in the coating, ultimately compromising its integrity.

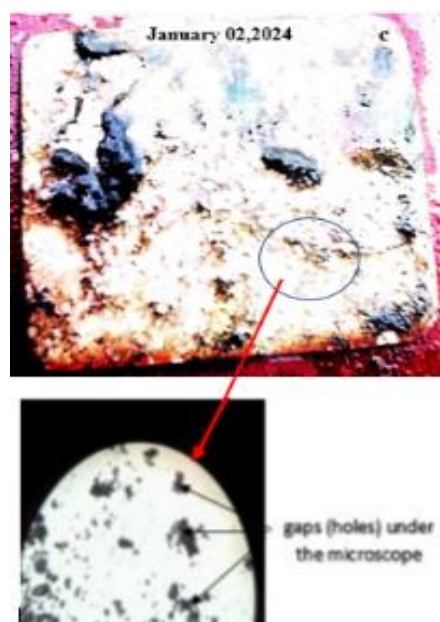


Fig. 10: Swelling of the antifouling paint and subsequent formation of surface gaps. Microscopic observations reveal that the paint undergoes progressive disintegration, leading to the appearance of holes in the coating structure [40]

In January 2024, bacterial colonization of the plate progressed from reversible to irreversible adhesion. The bacteria produced extracellular polymeric substances (EPS), mainly composed of proteins and polysaccharides, forming a biofilm matrix that stabilizes the attached microbial communities (Fig.9c) [47].

Additionally, a thin layer of filamentous green algae was observed extending across the left side and upper region of the plate, contributing to biofouling (Fig.9c).

These observations were compared with a biological study conducted on a plate retrieved from a mobile seawater filtration device operating in the port of Oran, Algeria (Fig.11) [11, 48]. That plate exhibited significant colonization by undesirable microorganisms, which increased drag forces on the device and hindered its mobility. Maintaining a constant speed under these conditions required higher fuel consumption, leading to elevated operational costs. As a result, frequent cleaning and maintenance were necessary, incurring considerable economic consequences. Over time, such biofouling contributes to reduced operational efficiency. This phenomenon is widely recognized as a serious challenge with substantial techno-economic implications for marine and industrial systems [49–51].



Fig. 11: Plate from an industrial seawater filtration device showing advanced paint degradation and replacement by biofouling organisms [37].

Environmental factors such as temperature, salinity, turbidity, light availability, and the physical characteristics of the substrate further facilitate the development and persistence of biofouling communities [52–55]

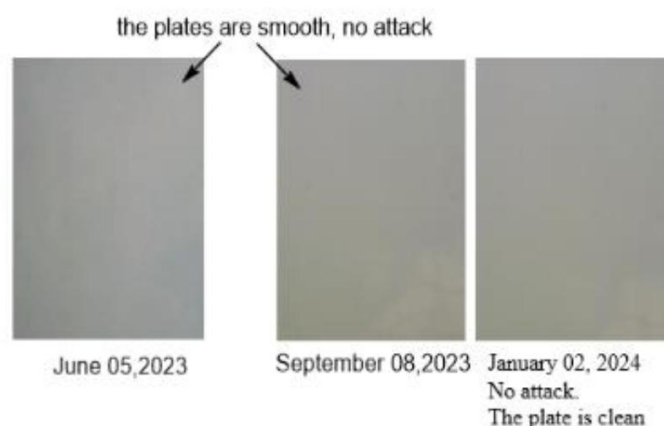


Fig. 12: Plates treated with the perfluorocoumarin-based surfactant.

The plate coated with paint containing the perfluorocoumarin surfactant shows no signs of degradation, indicating enhanced resistance to biofouling and environmental deterioration [40]

However, analysis of the plate coated with the hybrid surfactant (perfluorocoumarin) (Fig.11) reveals that no such surface degradation or conformational instability occurs. This is attributed to the ability of the surfactant chains to systematically self-assemble into micellar ring structures, which inhibit surface wettability. As a result, the coated surface exhibits outstanding antifouling performance and robust protection against biofouling (Fig.12) [56].

The fluorinated film formed by this surfactant demonstrates strong adhesion, a glossy finish, and superior resistance to corrosion. The incorporation of the coumarin moiety contributes to the mechanical reinforcement of the fluorinated coating, imparting anti-graffiti properties (Fig.12, January 2024). By optimizing the concentration of the perfluorocoumarin surfactant, the mechanical integrity of the coating can be further improved, limiting moisture penetration to the metal substrate and significantly extending the service life of the protected component.

CONCLUSIONS

The antifouling performance of the commercial Micron Extra EU paint was found to be suboptimal due to its limited surface coverage and susceptibility to microbial attachment and paint swelling. In response, a new hybrid surfactant combining fluorinated chains with a coumarin backbone was synthesized *and incorporated into marine coatings*. This formulation significantly enhanced antifouling performance by preventing biofilm formation and minimizing surface degradation. The improved effectiveness is attributed to the optimal conformation of perfluorinated chains and the chemical rigidity introduced by the coumarin core. The resulting coating also demonstrated anti-graffiti properties, excellent adhesion, and mechanical durability. Moreover, it exhibited strong resistance to corrosion and required no regeneration over extended periods. This hybrid coating offers a cost-effective, environmentally friendly, and laboratory-scalable solution for marine antifouling applications. Nonetheless, further investigations are needed to assess its long-term mechanical and chemical stability, particularly under real marine conditions and for large-scale industrial deployment.

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Data availability

All data generated or analyzed during this study are included in this published article.

Declarations

Conflict of interest

The authors declare that they have no conflict of interest.

Ethical approval

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