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Eco-friendly non-biocide-release coatings for marine biofouling prevention

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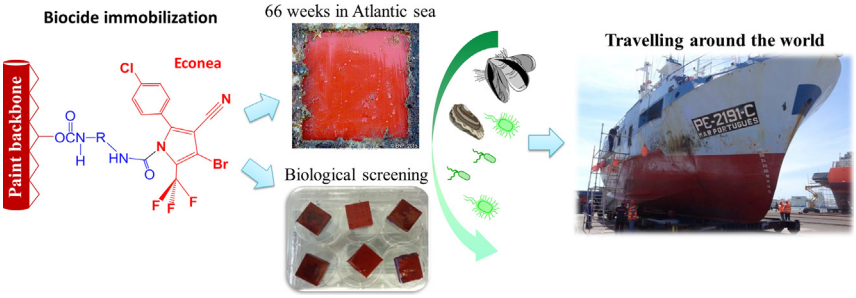
HIGHLIGHTS

- Marine biofouling, an unsolved economic and environmental burden
- Antifouling paints often release toxic and persistent antifouling agents.
- Isocyanate functional biocides with covalent binding ability were developed.
- Antifouling efficacy in real scenarios for marine paints with tethered biocides
- Pursuing eco-friendly antifouling strategies for the marine industry

GRAPHICAL ABSTRACT



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ABSTRACT

Environmental concerns have been changing the way of looking for solutions to problems. The hydrosphere, together with its biosphere, has been feeling the impact of many pollutants, used for instance in the marine industry for economic reasons or lack of knowledge of their effects. In particular biocides, applied as coatings in paints, are released into the waters becoming toxic and persistent extending their action to an area far beyond the initial coated surface they should protect. In order to minimize these side effects, two biocides, Irgarol (I) and Econea (E), were covalently attached to polyurethane (PU) and foul-release silicone based (PDMS) marine paints through an isocyanate linker. Their antifouling bioactivity was better in PDMS coatings, both for single (Econea) and combined biocides (E/I ratio = 1.5) with contents lower than 0.6 wt%. The treated samples remained almost clean after more than one year immersion in the Portuguese shore of the Atlantic Ocean, and after about 24 weeks under the tropical conditions of Singapore (Fouling rate < 1%). Complementary biofilm adhesion susceptibility tests against *Pseudoalteromonas tunicata* D2 showed adhesion reduction higher than 90% for PU formulations containing single biocides and close to 100% for PDMS with combined biocides. The eco-toxicity assessment evidenced a low environmental impact, in accordance with the European standards. In addition, shipping field trial tests showed the best antifouling performance for the Econea-based PDMS formulations (E = 0.6 wt%), which remained clean for about nine months in open seawaters, proving the efficacy of this non-release strategy, when applied under dynamic conditions.

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1. Introduction

Water, the primary resource for the growth and sustainability of our society, has ironically become one of the biggest challenges. The spontaneous colonization by aquatic micro/macroorganisms (freshwater/seawater) of submerged surfaces, known as biofouling, is responsible for serious economic and environmental penalties and health risks on several industrial activities, from marine transport (e.g. ships, vessels), offshore structures (e.g. oil platforms, aquaculture cages), water purification plants (e.g. filters, pipelines, valves, tanks) or even desalination processes (Bott, 2011; Chan and Wong, 2010). For instance, it may lead to efficiency losses of about 5% and premature substrate deterioration by biocorrosion up to 20% in cooling water circuits of power plants (Bott, 2011). Biofouling has been particularly hostile to the marine transportation business, as reflected on the costly consequences, around 150 billion USD per year, reported just for transport delays, hulls repair and maintenance (Nurioglu et al., 2015). But the impact of this natural phenomenon on shipping goes beyond this fractional cost. The primary undesirable effect of this bio-settlement on ships hulls is the generation of roughness, which can lead to drag resistance increases on ships up to 40% (Dahlbäck et al., 2010), and subsequent power penalties as high as 86% at cruising speed (Callow J. and Callow M., 2011). Therefore extra fuel consumption will be required to produce the needed energy to propel the vessels through the seawater *roads*. The United States Naval Sea Systems Command estimated that biofouling on ship hulls accounts for speed loss of about 2% and subsequent fuel cost increases ranging from 6 to 45%, depending on the size of the ship (Nurioglu et al., 2015), accompanied by an augment of Greenhouse gas (GHG) emissions (Banerjee et al., 2011). The International Maritime Organization (IMO) reported that, without corrective actions, gas emissions from world shipping fleets could increase from 150% to 250% by 2050, compared to the emissions in 2007. In particular, CO_2 emissions can even double by 2030, under extreme scenarios (IMO, 2009). In addition to the aforementioned drawbacks, marine biofouling is also the main vector for the introduction of invasive species (or non-native species) promoting potential side-effects to local biota (IMO, 2011; Flemming et al., 2011).

These substantial penalties of biofouling on industrial activities, with consequences on their sustainability and the environment, are the reason why the control and/or prevention of this bio-phenomenon are of paramount importance, constituting a focal point of modern research. A wide range of protection strategies have been exploited (Eduok et al., 2017; Nurioglu et al., 2015; Lejars et al., 2012). Hitherto, conventional antifouling technologies, mostly based on the controlled release of toxic substances into the immediate surroundings of the contaminated surfaces, seem to be the most effective strategy. For the marine industry, this has been achieved primarily by employing antifouling coatings. The polymeric framework of a coating can entrap biocides which are emitted, in a more controllable way, into the immediate surrounding area of the contaminated surface, thus killing or inhibiting the growth of potential fouling organisms. This antifouling strategy is well consolidated and commercially established, but, despite its recognized effectiveness, it has revealed significant limitations and/or drawbacks. Among those are the requirement of an effective mass transfer to ensure the efficiency of the antifouling agent, the incapacity of effectively prevent biofouling in all scenarios, and specially the intrinsic ecotoxicity of antifouling agents and their derivatives, which are usually associated to harmful effects on non-target organisms (Amara et al., 2018), leading to subsequent side-effects on aquatic ecosystems.

As a result, new rigid international regulations have been issued (BPD-Biocidal Product Directive, Regulation (EU) n° 528/2012-22) to ban some of the most effective agents (e.g. TBT) and scrutiny more (Amara et al., 2018). This tighter environmental protection legislation intensified the effort to the pursuit of non-toxic antifouling strategies. Several alternatives have been emerging, but up to now the most acceptable one is the biocide-free strategy, with particular interest for polysiloxanes (e.g. PDMS) based coatings with a low surface energy (~22 mN m^{-1}) and low modulus, suitable to minimize the adhesion of marine organisms on coated surfaces, mainly of hard-fouling (Eduok et al., 2017; Selim et al., 2017). However, the non-stick ability of polysiloxanes makes difficult its adhesion to substrates. Their relative poor mechanical properties contribute to being easily damaged, and to reduce their performance and service lifetime (typically 5 to 10 years), becoming only totally effective for fast moving vessels (>15–30 knots) (Lejars et al., 2012). Alternative contact bioactive strategies focused on the binding (tethering) of antifouling agents by covalent bonds in a polymeric matrix (Banerjee et al., 2011; Charnely et al., 2011; Kugel et al., 2011) have been proposed. A wide range of bioactive molecules has been tethered to different polymeric matrices, such as thermoplastic polyurethane and polyethyleneimine (PEI)-based coatings, thermoset siloxane, epoxy or polyurethane coatings. These approaches have been however mostly limited to biomedical applications, food industry and/or water purification systems (Banerjee et al., 2011), mainly due to three main reasons: low range of antifouling efficacy of the bioactive agents; compatibility with suitable polymeric matrices for marine environment, where high physicochemical resistant materials are required; and most of the used immobilization techniques still demonstrate to act partially by a releasing agents action (Kritzelr S. and Kritzelr M., 2013).

There is no doubt that the entrance in an environmental-friendly era requires efforts to convert these strategies into an acceptable and sustainable universal environmental friendly antifouling solution, beyond the emerging coatings generation development.

In compliance with this global aim, this work proposes a novel approach, based on the development of functional reactive biocides able to remain linked through covalent bonds to polymeric systems. Thus, the antifouling action will be provided by contact, in contrast with the conventional releasing strategies. The effectiveness of this eco-friendly strategy is firstly screened at a laboratory scale with biofilm adhesion tests on coated substrates with marine paints containing the fixed commercial biocides. The proof-of-concept is provided under real relative static conditions by field tests in a dock of coated prototypes, and at non-static conditions through ship field trial tests.

2. Materials and methods

2.1. Immobilization of biocides in marine paints

Irgarol® 1051 [*N′-tert*-butyl-*N*-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine], 96.0–99.0%, provided by BASF Chemicals, and Econea® biocide [(4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3 carbonitrile)], 98%, provided by Janssen PMP, were the selected antifouling agents to be immobilized (SI Fig. S1).

The developed non-release biocide method for the covalent immobilization of these biocides in marine coatings is described in detail elsewhere (Silva et al., 2016). The first step comprises the functionalization of the biocides with a reactive isocyanate (—N═C═O) (c.f. SI, Fig. S2), in order to allow further immobilized through covalent bonds to compatible polymeric matrices backbone.

The functionalization step starts with biocides dissolution in suitable solvents (15–30 wt%), butyl acetate and ethyl acetate p.a. (Sigma-Aldrich), for Irgarol and Econea biocides respectively. The biocidal solutions are added dropwise into a three-necked round bottom flask containing a diisocyanate reagent (e.g. 4, 4 diphenyl diisocyanate-MDI) at 40 ± 5 °C under mechanical agitation (300–400 rpm), and inert atmosphere conditions. After mixture, the reaction proceeds at stoichiometric conditions and for periods ranging from 2 to 10 h depending on the biocide content, after which is left to cool to room temperature, promoting the precipitation of functional biocides. Finally, the obtained biocides named as I-NCO (Irgarol—N═C═O) and E-NCO (Econea—N═C═O) are filtrated and dried in a Butchi R-210/215 rotovapor.

For the second step, the immobilization of biocides in polymeric matrices, two biocide-free commercial marine paints, gently provided by