Progress in Organic Coatings 77 (2014) 485–493

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Development of environmentally friendly antifouling paints using biodegradable polymer and lower toxic substances

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ARTICLE INFO

Article history:
Received 26 March 2013
Received in revised form 6 September 2013
Accepted 14 November 2013
Available online 12 December 2013

Keywords:
Environmental coatings
Antifouling
Active substances
Microfouling

ABSTRACT

The development of new antifouling coatings with respect to the marine environment is actually crucial. The aim of the present work is to concept an erodible paint formulated with biodegradable polyester as binders and which combines two modes of prevention: chemical and physical repelling of biofouling. This system is principally dedicated to disturb durable settlement of microfouling. Each component was chosen according to its specific properties: chlorhexidine is a bisdiguanide antiseptic with antibacterial activity, zinc peroxide is an inorganic precursor of high instable entities which react with seawater to create hydrogen peroxide, Tween 85 is a non ionic surfactant disturbing interactions between colonizing organisms and surface. Obtained results highlighted the interest on mixing such molecules to obtain a promising coating with lower toxicity than traditional systems.

1. Introduction

Marine biofouling can be defined as the undesirable accumulation of microorganisms, algae and invertebrates on submerged unprotected substrates. Fouling causes severe problems on both dynamic and static structures (speed reduction of vessels, increase of fuel consumption, increase of hull maintenance etc.). Over the long history of fouling prevention a variety of methods have been used (tar, pitch, copper sheathing etc.) [1,2]. The first antifouling paints appeared in the mild 19th century, containing copper, arsenic or mercury oxide as toxicants dispersed in linseed oil or shellac. However, the most successful antifouling paints in term of long time efficiency have been tributyltin (TBT)-based antifouling paints. Due to environmental concern, these TBT-based systems have been totally banned since 1st January 2008. During the last decade, modern antifouling alternatives consist of coatings containing polymer matrix (acrylic and vinyl resins sometimes blended with rosin) and various kinds of biocides which come into contact with fouling organisms [3]. They include organic molecules called booster biocides and mineral compounds such as cuprous oxide and, less commonly, cuprous thiocyanate. Booster biocides are generally toxic against aquatic plants and animals [3,4]. It has long been widely used as algaecides, bactericides and fungicides. Bao et al. suggest that some of these biocides could even be more toxic than tributyltin oxide (TBTO) to certain biota (cyanobacteria, diatoms) [5]. For example, Irgarol, zinc pyrithione and copper pyrithione were more toxic than TBTO on the growth of the two cyanobacteria *Chroococcus minor* and *Synechoccus* sp., the diatoms *Thalassiosira pseudonana*. Mineral copper was relatively less toxic, however the risk of copper toxicity on the marine ecosystem should not be neglected [3,5,6]. Toxicity of current anti-fouling paints is largely highlighted [7,8]. Hence, there is a real need to develop non-toxic technologies [9].

Non-toxic antifouling strategies include both physical and chemical concepts [10]. Recent research has focused on non-release coatings [11–13]. These approaches are mainly based on controlling physicochemical and mechanical properties such as surface roughness, the elastic modulus, the topographies or the wettability of the surface, which impact on the interactions between marine organisms and the surface [14]. Another antifouling strategy would be to develop formula based on novel biocides (Medetomidine and Econea) or on natural compounds [4,9,15]. For example, rosin-based coatings loaded with low concentrations of ivermectin, a macrocyclic lactone, were found to be effective in preventing colonization by barnacles [16]. Green antifouling compounds from microorganisms, seaweeds and aquatic plants, marine invertebrates and from terrestrial natural products have been extensively investigated [17]. Nevertheless, their use into commercial paints is rather slow because the issue of supply has always been a major obstacle [18]. Moreover, paints must reach and maintain a sufficient

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0300-9440/$ – see front matter.
http://dx.doi.org/10.1016/j.porgcoat.2013.11.012

concentration of the active ingredients to give the desired effect. So, an optimization of formulations and biocide release profiles is essential. For example, Bellotti et al. have shown that antifouling paints with zinc "tannate" are promising, nevertheless, antifouling efficiency was dependent on the formulation: the matrix and the plasticizer employed modified the antifouling activity [19].

A critical parameter to control the release of active ingredients and antifouling efficiency concerns the paint erosion. Erosion can be controlled by the nature of the binder [20,21]. So, polyacrylic resins bearing hydrolysable functions have been developed as tin-free alternatives paints. The nature of hydrolysable pendant groups is variable: copper-, zinc-, trialkylsilyl-, trialkyltitanate, ammonium salt or poly(acide lactic) [21–26]. In our research group, biodegradable polymers (polyesters based on polycaprolactone) have been investigated as a potential binder to obtain controlled depletion paints (CDP) [20,27]. Results have shown that poly(ε-caprolactone-co-δ-valerolactone (P(CL-VL)) are good candidates to obtain CDPs taking into account industrial constraints (life-time, stability, biocide release etc.).

This present study focuses on the use of P(CL-VL) as a biodegradable binder combined with no conventional biocides currently used in antifouling paint. Three actives substances are chosen to produce a biodegradable coating combining chemical and physical action and targeting the microfouling. Chlorhexidine, an antibacterial compound, which is used in dentistry as an anti-dental plaque agent [28,29]. Zinc peroxide (ZnO_2) is a deterrent that can cause damage to cells and is commonly used for disinfection [30–32]. Detergents such as Tween (polyethylene glycol sorbitan trioleate) (Tween 85) are able to disturb interactions between colonizing organisms and the surface, to decrease bacterial adherence and to favour their release under flow stress. In a previous study, we have highlighted the additive action of three active substances incorporated in polyacrylic paint [33]. No synergistic effect between chlorhexidine, Tween 85 and zinc peroxide has been observed, nevertheless an interesting antifouling activity has been observed by blending the three molecules and by combining the chemical and physical effects. So, the aims of this study are: (i) to evaluate the efficiency of these active substances incorporated into polyester matrix, to concept a new biodegradable coating, (ii) the study of its biodegradation, (iii) the evaluation of its efficiency against -micro and -macrofouling. Indeed, antifouling efficiency (biological activity, lixiviation) and ecotoxicity are parameters which could be greatly impacted by the nature of polymer matrix (polyacrylic versus polyester) and the formulation type (varnish versus paint).

In a first time, the biological activity of varnishes based on biodegradable polyester and active substances against marine micro-organisms and their ecotoxicity are studied. Then, they are incorporated and evaluated in an antifouling paint. A preliminary evaluation of the interest to targeting microfouling for obtain efficient paint will be addressed.

2. Materials and methods

2.1. Chemical products

Tween 85 (polyethylene glycol sorbitan trioleate), chlorhexidine, zinc peroxide, ε-caprolactone (CL), δ-valerolactone (VL) and tetrabutoxytitane $Ti(OBu)_4$ were purchased from Acros Chemical. They were used as received without further purification. Zinc pyrithione, dichlofluanid and copper thiocyanate were supplied by Nautix Company.

2.2. Binder

The polyacrylic binder was purchased from ZENECA. It is a blending of acrylic copolymer poly(methyl methacrylate-co-butyl methacrylate) (PMMA-PBMA) with rosin: a mixture of abietic and dehydroabietic acid obtained from the exudation of pine and fir trees.

The biodegradable polymer, poly(ε-caprolactone-co-δ-valerolactone) 80/20 (Mn = 25 000 g/mol, polydispersity index = 1.2) was synthesized (Fig. 1) and validated as a potential binder in previous studies [20,27]. The hydrolysable backbone led to a slow hydrolytic degradation of the immersed binder in demineralized water at 20 °C and to the control of erosion.

2.3. Formulation of varnishes

To evaluate the efficiency of actives substances against micro-organisms, varnishes were formulated. They are simplified coatings and are composed only by binder and active substances. Varnishes were prepared from a solution containing 40% (w/w) of the P(CL-VL) binder, 10% (w/w) of the active substance and 50% (w/w) of the diluting agent (xylene). A layer of wet film (200 μm thick) was deposited with an automatic film applicator (ASTM D823 Sheen instrument) on a polycarbonate support. Then the specimens were dried at 20 °C until they achieved a constant weight. An unloaded varnish was used as negative control.

2.4. Bacterial strains and culture conditions

The marine bacteria used, are *Bacillus* (4J6) *and Pseudoalteromonas* (3J6), which were grown on a rich medium: Marine Broth (Bacto Marine Broth 2216, Difco). It contains (%): peptone 0.5, yeast extract 0.1, $FeC_6H_5O_7$ 0.01, NaCl 1.945, $MgCl_2$ 0.59, Na_2SO_4 0.334, $CaCl_2$ 0.18, KCl 0.055, Na_2CO_3 0.016, KBr 0.008, SrC 3.4×10^{-3}, NaF 0.24×10^{-3}, $Na_2Si_3O_7$ 3.4×10^{-3}, H_3BO_3 2.2×10^{-3}, NH_4NO_3 0.16×10^{-3}, Na_2HPO_4 0.8×10^{-3}. Planktonic cultures were maintained at 20 °C whilst shaking. These bacteria were used because they are pioneer adherents.

Strains were isolated from the surface of a glass cover immersed in natural seawater (Morbihan gulf, France) for 6 h. Both strains are hydrophilic. 3J6, a gram negative bacteria, was affiliated to the *Pseudoalteromonas* genus [34]. Its 16S rDNA sequence (GenBank entry FJ966949) is the most closely related (95.5% identity) to that of the *Pseudoalteromonas* sp. SM9913, strain [35] and belongs to a new species. The gram positive bacteria 4J6 clustered with the genus *Bacillus* (100% similarity) [34]. Both bacteria were negatively charged at the pH of the seawater.

2.5. Evaluation of antibacterial activities

The zone of inhibition assay on solid media was used for determination of the antimicrobial effects of varnishes against

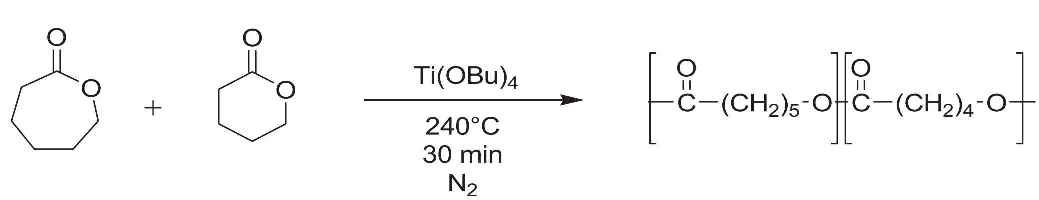

Fig. 1. Chemical structure of poly(ε-caprolactone-co-δ-valerolactone) 80/20 obtained by ring opening polymerization.