Contents lists available at ScienceDirect





Progress in Organic Coatings

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

Field study of the long-term release of block copolymers from fouling-release coatings



A. Camós Noguer^{a,b}, S.M. Olsen^b, S. Hvilsted^a, S. Kiil^{a,*}

^a Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Building 229, 2800, Kgs. Lyngby, Denmark
^b Department of Fouling Release Systems, Hempel A/S, Lundtoftegårdsvej 91, 2800, Kgs. Lyngby, Denmark

ARTICLE INFO

Keywords: Fouling-release coatings Block copolymers Oils Release

ABSTRACT

The addition of block copolymers (i.e. oils) is a common technique to enhance the biofouling-resistance properties of poly(dimethylsiloxane) (PDMS)-based fouling-release coatings. These copolymers diffuse from the bulk to the surface of the coating, thus modifying the properties of the surface and providing fouling-resistance properties. Upon release, dissolution or degradation of copolymer molecules at the surface, new molecules can diffuse from the bulk of the coating and cover the surface. Therefore, the long-term performance of these coatings is dependent on the stability and release rate of copolymer molecules from the surface.

A method was developed to quantify the concentration of PDMS-based block copolymers from fouling-release coatings. About 300 experimental coatings exposed to seawater for up to 5.2 years were included in the analysis. The results showed that the loss of copolymer (in % on a weight basis) is significantly higher in warm waters, while the initial copolymer concentration in the coating does not have any effect for copolymer concentrations between 1 and 7 wt%. In short-term exposure, it was found that loss of copolymer was much higher in coatings containing small amounts of an organic biocide (copper pyrithione). Conversely, biocide-containing coatings displayed larger copolymer retention values in long-term experiments. Opposite results were obtained for biocide-free coatings, suggesting that the addition of the organic biocide alters the release profile of copolymers from fouling-release coatings. Finally, the potential of long-term field-studies is discussed, as compared to short-term laboratory experiments usually performed within fouling-release coatings studies.

1. Introduction

After the ban of tributyltin self-polishing copolymer (TBT-SPC) coatings was approved by the International Maritime Organization (IMO) in 1998 [1], the coatings industry focused on developing environmentally-friendly biocide-free coatings [2,3]. Hydrophobic polydimethylsiloxane (PDMS)-based coatings, usually known as fouling-release coatings (FRC), emerged as a solution due to its unique foulingrelease properties. These have been attributed to its low critical surface energy (γ_c) [4], low elastic modulus (E) [5], low glass transition temperature (Tg) [6] and smooth surface [7] and result in weak adhesion between the adhesives secreted by biofoulants and the surface of the coating [8-10]. Consequently, the biofouling film is detached (i.e. released) when the vessel navigates at moderate speeds (about 15 knots) [11]. However, its hydrophobic surface favours the adhesion of some marine organisms, which cannot always be completely removed by hydrodynamic forces. It has been shown, for example, that diatoms cannot be released at speeds as high as 30 knots [3].

To improve the biofouling-release properties of FRC, "oils" (mostly

polysiloxane-based fluid additives) have been traditionally added [3,8]. These oils consist of block copolymers containing different chemical moieties. The mostly employed polymers have been fluorinated- and polyether-based polymers, as well as phenyl-modified polysiloxanes [3]. For example, poly(tetrafluoroethylene) (PTFE) and poly(ethylene glycol) (PEG) have been extensively used. In addition, it has been shown that copolymers based on other polymers [12], zwitterions [13] or peptides [14] can also provide non-fouling properties when added as additives to different coatings. The effect of the chemistry and structure of various oils on the adhesion strength of different biofouling species have been studied. The results show that the adhesion strength reduction is highly dependent on the chemistry of the used oil as well as the biofouling organism investigated [12,15].

These oils segregate from the bulk and cover the surface of the coatings upon immersion [16,17]. On the surface of the coatings, one of the copolymer blocks acts as an anchor to the surface and imparts stability to the copolymer molecule [18,19]. The other block(s) of the copolymer is usually extended to seawater (sometimes in the form of a polymer brush) and confers non-fouling (i.e. repellence) properties

http://dx.doi.org/10.1016/j.porgcoat.2017.07.001

^{*} Corresponding author. E-mail addresses: alno@kt.dtu.dk (A. Camós Noguer), stmo@hempel.com (S.M. Olsen), sk@kt.dtu.dk (S. Kiil).

Received 6 February 2017; Received in revised form 4 July 2017; Accepted 5 July 2017 0300-9440/ © 2017 Elsevier B.V. All rights reserved.



[18]. Consequently, the addition of small amounts of these additives result in the modification of the physicochemical properties of the surface with a very small influence on the bulk properties of the coating [12,20,21].

Nonetheless, it has been suggested that these oils can be "washed away" (i.e. released or dissolved in seawater) and/or degraded at the surface of the coating. When a molecule from the surface of the coating is removed, a new molecule diffuse from the bulk of the coating to cover the surface [20]. This "self-healing" process can take place as long as copolymer molecules are available in the bulk of the coating. The properties of these coatings are hence expected to deteriorate upon shortage of copolymer molecules in the bulk. The anchoring capabilities of this kind of surface-active copolymers on different polymeric matrices have been studied. In these investigations, different surfactants and block copolymers have been added to PDMS (or other polymeric matrices) and the wettability of the surface has been studied after soaking the samples in water for different exposure times [22-27]. For example, Seo and Lee [22] added a surfactant based on PEG to PDMS. After immersion in water for 18 days, significant changes in wettability of the PDMS surface were observed and attributed to additive depletion. Similarly, a PDMS-PEG-based copolymer was added to PDMS by Kim et al. [23] and samples of the material were soaked in water for 35 days. Slight differences on the surface of the PDMS samples after exposure were also reported. Madadi and Casals-Terré [26] could see significant differences in hydrophilicity in PDMS samples modified with non-ionic surfactants, when the samples were exposed to contact with water for short periods. Finally, Fatona et al. [27] analysed PEG-based surfactants and copolymers with different hydrophobic groups added to PDMS elastomers and soaked for 20 h in water. They showed that the stability of these additives on the PDMS surface was significantly higher when copolymers containing a PDMS block were used, compared to those containing an alkyl hydrophobic group. Nonetheless, the exposure times investigated in the aforementioned studies are not representative for fouling-release coatings, which are exposed to seawater over several years. Hence, the usefulness of such experiments on the studied coatings is limited. Recently, some novel PDMS-based coatings containing both the traditional "oils" and biocides have been commercialized. The addition of small amounts of biocides is suggested to improve the non-fouling properties of the coatings (specially in idle conditions). The use of organic biocides such as zinc pyrithione, Zineb and Irgarol together with fouling-release "oils" has been described in different patents [28,29]. However, the addition of biocides could significantly influence the behaviour and release of these copolymers, both due to the presence of biocide in the film and the leached layer that is generated upon its dissolution.

It is well recognized that addition of block copolymers (i.e. oils) to fouling-release coatings enhances the fouling-resistance of these coatings to a great extent. Therefore, being able to quantify and control the processes that dictate the release rate at the surface of the coating is crucial for the development of robust long-lasting coatings. With the aim of better understanding the stability of polymeric-based additives in silicone coatings, up to 300 experimental fouling-release coatings exposed to seawater for different periods of time have been analysed. The experimental coatings consist mainly of a PDMS binder and a surface-active additive, a PDMS-PEG-based copolymer. First, a method to quantify the amount of additive present in coatings has been developed inspired by the work of Reynier et al. [30]. Then, the experimental fouling-release coatings, exposed to seawater for different times have been analysed and compared to coatings exposed in a laboratory rotor in controlled conditions. The influence of different variables/ parameters on the release of these copolymers has been studied. These variables include: (1) temperature of seawater. (2) the chemistry of the crosslinker. (3) the molecular weight (M_w) of the copolymer and the initial concentration of (4) biocide and (5) copolymer in the coating. Finally, the influence of the aforementioned variables on the release/ loss of copolymer from PDMS-coatings is discussed. The conclusions drawn from this long-term field-study possess the advantage of relying on results obtained from coatings immersed in real seawater conditions, in comparison to traditional short-term laboratory experiments. These results obtained provide some insights and findings, which might not be available when short-term experiments in ideal conditions are employed.

2. Materials and methods

2.1. Materials

Di-hydroxy terminated polydimethylsiloxane (4000 cSt) was purchased from Dow Corning. Vinyl tris(methyl ethyl ketoxime) silane (crosslinker I), a pre-polymerized ethoxysilane crosslinker (crosslinker II), and a methoxy functional vinyl siloxane oligomer (crosslinker III) were purchased from Evonik Industries and can be seen in Table 1. Surface-treated fumed silica (SiO₂, average particle size about 15 nm) was also received from Evonik and red iron oxide (Fe₂O₃) pigment Bayferrox 130 M from Lanxess. Two different PDMS-PEG-based block copolymers (copolymer A and copolymer B) were obtained from different suppliers with $M_w = 1.000-10.000$ g/mol and triblock ABA structure. The molecular weight of copolymer A was ~75% larger than of copolymer B. Copper pyrithione (CuPT), also known as copper omadine, was obtained from Lonza.

2.2. Formulation of coatings

The coatings were prepared by mixing three components: (1) base (containing binder, solvent, silica, pigment and CuPT), (2) crosslinker (I, II or III) and (3) a PDMS-PEG-based copolymer (A or B). The base was prepared by mixing silanol-terminated PDMS with xylene (about 15 wt%) and with a series of components. Iron oxide (Fe₂O₃) and fumed

Download English Version:

https://daneshyari.com/en/article/4999130

Download Persian Version:

https://daneshyari.com/article/4999130

Daneshyari.com