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Erosion of a model rosin-based marine antifouling paint binder as studied with quartz crystal microbalance with dissipation monitoring (QCM-D) and ellipsometry

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Abstract

In this study two surface sensitive methods, i.e. quartz crystal microbalance with dissipation monitoring (QCM-D) and ellipsometry, were used for erosion measurements of a rosin-based marine antifouling paint binder. Thin films of the binder were applied on sensor surfaces by the means of spin-coating and the effect of water velocity over the paint film, water temperature or ionic strength on erosion was investigated. Both the acoustic QCM-D model and the optical ellipsometry model gave comparable erosion results. The initial 2–50 nm rapid erosion of the top layer was followed by steady-state erosion rate until end of experiment. For example, the steady-state erosion rate was 12 nm/24 h in artificial seawater at 23 °C and with a flow of 200 μl/min over the paint surface as measured with QCM-D. The erosion rate increased with increased velocity and increased temperature. Ionic strength had no effect on the erosion rate of this model binder. At low water velocities the surface layer was highly dissipative indicating a water filled surface top layer or the formation of deposits on the surface. New characterization techniques that are able to study the erosion mechanisms on the nanometre scale are sought for as the binders get more technically complex containing, for example, nanoparticles or enzymes. Surface sensitive methods could be used to rapidly screen the effect of different binder chemistries or paint additives on the erosion during the paint development process.

Keywords: Antifouling coatings; Erosion; Quartz crystal microbalance with dissipation monitoring and ellipsometry

1. Introduction

A modern antifouling paint should perform as a controlled-release pharmaceutical formulation. There should be no burst effect of bioactive substances from a newly painted hull and there should be a well-controlled delivery at a biological active concentration over a period of time. It should be stressed that the time of delivery is years in the case of an antifouling paint, which should be compared to hours or days in the case of a pharmaceutical formulation. This is a major technical challenge that is further complicated by the complex chemistry of a modern paint formulation, which makes predictions of the structure of the paint film upon evaporation of the solvent very difficult. It is also quite difficult to study the structure and dynamics of molecules in the dried film in a non-invasive manner and one is often left with studying macroscopic effects such as release of bioactive substances and swelling of the paint film on the supramolecular level and upwards. The general analytical procedures are based on simple gravimetric analysis or high vacuum techniques such as scanning electron microscopy (SEM). Even though SEM is a powerful technique it should be stressed that the drying process could result in distortion of the paint structure. With new high resolution methods capable to conduct measurements in seawater the understanding of processes such as erosion could be better described.

The most comprehensive work on understanding erosive mechanisms of self-polishing and ablative coatings has been carried out by Kiil and co-workers at Technical University of Denmark [1–6]. Based on reaction rate results and mathematical modelling they have presented both new mechanisms and models describing the erosion of self-polishing copolymers and rosin-based antifouling paints. When a rosin-based paint formulation is exposed to seawater the reaction starts with water penetrating into the top layer of the coating. The structure of the water filled top layer, which usually is termed “leached” or “erosive layer”, controls the erosion rate of the paint film. The

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formation, structure and thickness of the erosive layer depended on paint parameters such as type of rosin, additives in the paint and on external parameters such as water salinity, temperature and pH. The erosion rate in the studies by Kiil et al. was determined by two different methods, i.e. one gravimetrical method and one method based on flame atomic absorption spectroscopy (FAAS) analysing the total amount of Cu^{2+}, Mg^{2+} and Zn^{2+} released from the metal-containing rosin derivatives. Based on their results they proposed a complex reaction mechanism rather than a diffusion controlled mechanism. The conversion of the Zn-resinate to Mg- and Na-resinate upon contact with seawater had a significant effect on the erosion rate. Moreover, the release rates observed for different metal resinates varied from 5 μg/(cm^2 day) for Cu-resinate, 22 μg/(cm^2 day) for the Zn-resinate and 35 μg/(cm^2 day) for the Mg-resinate at 25 °C and pH 8.2. It should be noted that the steady-state erosion rate was observed first after about 20 days of immersion. The initial erosion rate was roughly twice the steady-state erosion rate.

In another study in which important paint properties were correlated to antifouling activity the only factor having significance was the erosion rate [7]. It is interesting to note that the authors did not observe a correlation between biocide release and antifouling activity, a result stressing the need for a better scientific understanding of phenomena which have a decisive role in antifouling activity. The same authors also developed a scanning electron microscopy (SEM) method coupled with X-ray analysis (EDX) in order to study the erosion and distribution of molecules in the paint film [8]. They noted that with a better distribution of active molecules in the paint the release could be decreased with the same antifouling activity. Although SEM is a very powerful technique it is still a high vacuum method which gives useful information about dry film structure, but the fine structure of the leached layer could be distorted during the drying process and complementary methods are sought for.

In this study we introduce modern thin film characterization techniques such as ellipsometry and quartz crystal microbalance with dissipation monitoring (QCM-D) with the aim to increase the scientific understanding of erosive mechanisms in eroding marine paints. Ellipsometry is a well-established optical analytical method, especially for determining film thicknesses down to the nm resolution [9,10]. No need for molecular labeling it is quick and fairly quantitative are some of the advantages of the method [11].

The QCM-D technique allows simultaneous time resolved measurements of the amount of mass on the crystal and the dissipative properties of the layer [12,13]. The acoustic QCM-D technique has grown rapidly the last decade including studies of enzymatic degradation of thin polymeric films to measurements involving micellar systems, self-assembling monolayers and their phase transition behavior, molecularly imprinted polymers, chemical sensors, polymer film swelling and biopolymer adsorption and cross-linking [14–20].

2. Experimental

The rosin-based model paint binder was obtained from Hempel A/S, Lyngby, Denmark (polishing model binder 1) and according to the product data sheet it contains the following components: colophony or rosin (CAS# 8050-09-7) 15–20%, ethyl benzene (CAS# 100-41-4) 15–20%, triisopropyl silyl acrylate (CAS# 157859-20-6) 0.15–0.20% and xylene (CAS# 13330-20-7) 15–20%. The model binder was further diluted 1:10 in xylene before used.

2.1. Erosion studies with QCM-D

In summary, the QCM-D technique is an acoustic method where a quartz crystal is set in lateral resonance oscillation with a predefined frequency (f). Simultaneous frequency (f) and dissipation (D) measurements are made by periodically switching on and off the ac-voltage over the crystal. The decay signal is recorded and fitted to an exponentially damped sinusoidal curve. The total mass on the crystal (g cm^{-2}) can be calculated from Eq. (1) by the frequency shift (Δf) using the Saurbrey equation [21], provided that the mass is evenly distributed, does not slip on the sensor surface and is sufficiently rigid and/or thin to have negligible internal friction. C_f is the mass sensitive constant (e.g. 17.7×10^{-9} g cm^{-2} Hz^{-1}), n_r is the shear wave number, ρ_{rosin} is the density (g cm^{-3}) of the rosin, δ_{rosin} is the thickness of the layer and m_{rosin} is the mass per unit area (g cm^{-2}) of the layer. As evident from Eq. (1) the erosion is possibly to measure if the density of the layer is known. Based on literature date we have used a density of 1.07 g cm^{-3} for all calculations:

$$-\frac{C_f}{n_r}\Delta f = \rho_{rosin}\delta_{rosin} = m_{rosin} \qquad (1)$$

In addition the decay time (τ) of the sensor crystal after the driving electric current is shut off is measured and is used to calculate the dissipation (D), Eq. (2):

$$D = \frac{1}{\pi f \tau} \qquad (2)$$

The dissipation gives valuable information about the damping or mechanical properties of the layer on the crystal. A very rigid material will have an increased decay time, and consequently, a low dissipation (D). Vice versa, a viscoelastic/soft material will result in fast damping of the sensor crystal, i.e. a short decay time and higher dissipation.

Coatings were applied on the sensor surfaces via spin-coating technique. The paint binder solution was spin-coated on quartz crystal sensor surfaces by applying 50 μl of the solution at 2000 rpm for 1 min. This procedure resulted in about 100 nm thick coatings on the sensor surfaces. Erosion was studied in two different ways. First, the paint-coated sensor surfaces were placed in 50 ml beakers and 15 ml distilled water or artificial seawater was added. At certain time intervals the sensor surface was withdrawn, washed with distilled water and dried with nitrogen. After at least 5 h of drying in an exsiccator the resonance frequency was measured in air. The erosion was calculated using Eq. (1) (reference frequency was the empty crystal). It should be stressed that this method is a simple gravimetrical method and does not reveal either the time resolved erosion nor the wet coating properties but was performed to verify that we had no saturation effects in the QCM-D chamber due to low rosin solubility.