Polystyrene films as barrier layers for corrosion protection of copper and copper alloys

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ARTICLE INFO

ABSTRACT

Dip-coated polystyrene layers of sub-micrometre thickness (85–500 nm) have been applied on copper and copper alloys (aluminium brass, copper–nickel 70/30), as well as on stainless steel 304, and produced an effective barrier against corrosion and adhesion of corrosion-relevant microorganisms. According to the dynamic wettability measurements, the coatings exhibited high advancing (103°), receding (79°) and equilibrium (87°) contact angles, low contact angle hysteresis (6°) and surface free energy (31 mJ/m^2). The corrosion rate of copper–nickel 70/30 alloy samples in 3.5% NaCl was as low as 3.2 μm/a (44% of that of the uncoated samples), and in artificial seawater was only 0.9 μm/a (29% of that of the uncoated samples). Cell adhesion was studied by fluorescence microscopy, using monoculture of Desulfovibrio alaskensis. The coatings not only decreased the corrosion rate but also markedly reduced the number of bacterial cells adhered to the coated surfaces. The PS coating on copper gave the best result, 2×10^3 cells/cm^2 (1% of that of the uncoated control).

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1. Introduction

Corrosion causes severe damage worldwide. The presence of corrosion-relevant microorganisms initiates biofilm formation; under these layers the metal surface starts to corrode. This is referred to as microbial corrosion or microbially influenced corrosion (MIC). Since MIC usually starts up under a developed biofilm, the strategies to control it are strongly related to the inhibition of microbial adhesion. Two different approaches are in application: 1) use of inhibitors and biocides; and 2) modification of surfaces by coatings.

A typical occurrence of MIC in the energy sector is the fouling and corrosion of condenser tubes of the cooling circuits of power plants. Most commonly, MIC is mitigated by chlorination, ferrous iron treatment and mechanical cleaning by circulating sponge balls. These are more or less effective methods, but even so, periodic shut-downs are unavoidable due to the need of maintenance and cleaning by hand [1–3].

Nanocoatings offer a new alternative solution of equal or better efficiency, being more cost-effective and implying less environmental load [4]. Self-assembled monolayers (SAM), Langmuir–Blodgett (LB) films and other organic thin films with the thickness of a few nanometres have been investigated and used for a long time in corrosion protection and against biofouling. The first SAMs were thiols on gold surfaces [5]. Since then, many different compounds on different metals and alloys have been proven to be effective against corrosion. The list includes thiols [6–19], amines [12], phosphates [20], sulfates [21], thiosulfates [22], carboxylic acids [23–29], hydroxamic acids [29–31], amino acids [32–34], phosphonic acids [29,35], sulfonic acids [29], silane derivatives [36], as well as heterocyclic and other compounds [16,37–44].

Our previous results with carboxylic, hydroxamic, and phosphonic acids applied in SAM nanocoatings proved the usefulness of these molecular layers as barriers against corrosion and microbial cell adhesion [45–51]. Recently, the focus of our research moved towards thicker polymer coatings. Out of the several possibilities, polystyrene (PS) was chosen as a model polymer in our experiments. The reasons for this choice are that:

a. PS is ubiquitous, available in large quantities as unprocessed waste;
b. it is non-toxic;
c. it is non-biodegradable;
d. it is inexpensive;
e. it is a simple, non-exotic polymer;
f. it can be further functionalised;

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g. it is well soluble in some common, inexpensive, non-toxic solvents;
h. its surface free energy [52] is close to the minimum biofouling value on the Baier-curve [53], predicting low cell adhesion.

As part of our overall endeavour to screen out potential candidates for efficient protective nanolayers, in this study we demonstrate a quick-test for monitoring the efficiency of PS nanocoating barrier layers against corrosion of copper and copper alloys as well as stainless steel 304, used as the materials of heat exchangers of power plants. Since in heat exchangers operating partly with seawater biofouling is a phenomenon occurring in parallel to, inseparable from corrosion, cell adhesion tests with *Desulfovibrio alaskensis* monoculture – as model microorganisms – were also conducted.

2. Materials and methods

2.1. Substrates

Pure (99.99%), plane-parallel, polycrystalline Cu samples of $14 \times 9 \times 2$ mm^3 dimension were polished by a P220 grit sandpaper. Tube section samples of aluminium brass (Al-b; composition: 76.447% Cu, 21.115% Zn, 2.166% Al, 0.046% Fe, 0.040% V), copper-nickel 70/30 (CuNi; composition: 66.660% Cu; 31.411% Ni; 0.829% Mn; 0.692% Fe; 0.053% Cr) [54] and stainless steel type 304 (SS; composition: 68.973% Fe; 18.371% Cr; 9.299% Ni; 1.680% Mn; 0.488% Si; 0.365% Mo; 0.302% Cu; 0.056% V; <0.080% C) [55] were of $12 \times 10 \times 1.3$ mm^3 dimension and 11 mm inner and 13 mm outer radii of curvature, respectively. These were not polished due to the difficulties arising from their geometry. For thickness measurements, silicon wafers were used as substrates.

2.2. Cleaning and pre-treatment

As proven indispensable [56,57], metal samples were degreased with acetone, and oxidized in a two-step pre-treatment consisting of a 5 min ultrasonic bath in 14 mM HNO$_3$, followed by a 5 min ultrasonic bath in 5% H$_2$O$_2$.

2.3. SAM coatings

Cleaned and pre-treated copper and alloy substrates were dipped into 2.0 mM solutions of *n*-octadecane 1-derivatives: octadecanohydroxamic acid (C18N) and octadecylphosphonic acid (C18P) in dichloromethane (DCM), for 1, 5 and 24 h. The coated samples were rinsed with pure solvent to remove any non-specifically bond, excess material, and were dried in air or in a stream of nitrogen.

2.4. Dip-coated PS

Cleaned and pre-treated copper and alloy substrates were immersed/withdrawn into/from solutions of atactic PS in DCM, at three different concentrations (10, 30 and 50 g/L) with a rate of 10 mm/s. Two PS sources have been used, H-type and T-type, differing in their average molar mass and dispersity (H-type: $M_n = 74,800$ and $Đ = 2.30$; T-type: $M_n = 88,700$ and $Đ = 2.84$).

2.5. Contact angle measurements

A Wilhelmy-type [58] digital surface tensiometer (Nima) was used. Samples were automatically dipped into and pulled out from water with a rate of 10 mm/min, while the apparent weight change of the target sample was registered. The contact angles were retrieved by inputting the cross sectional dimensions of the samples and the surface tension of the water. Ultrapure (MilliQ) water was used in the experiments.

2.6. Layer thickness measurements by ellipsometry

Thickness measurements were carried out close to the upper edge of the PS coating. The spectroscopic ellipsometer used (MM-16, HORIBA Jobin Yvon) was equipped with a non-rotating, liquid crystal compensator. The parameters of the measurements were: spectral range of 430–850 nm; angle of incidence 65°; spot size 1 mm. Fitting the thickness and refractive index to the measurement data was done with the DeltaPsi2™ software of the instrument.

2.7. Layer thickness profile determination by AFM

Parallel lines were scratched with a diamond tip in the PS coatings on Si along the dipping direction, perpendicularly to it, and the step heights were measured by a NanoScope® Dimension™ 3100 AFM apparatus (Digital Instruments/Veeco) equipped with a silicon nitride cantilever, operating in contact mode.

2.8. Corrosive liquids

Coated and uncoated metal samples were dipped in unstirred, non-deoxygenated solutions of 0.1 M Na$_2$SO$_4$ for 28 h, 3.5% NaCl solution for one week, and artificial seawater (ASW) for one week, respectively. ASW was prepared according to the recipe of Kester et al. [59]. Its composition is presented in Table 1.

2.9. Corrosion measurements by ICP–OES

The metal ion concentrations in the aqueous solution dissolved in the course of corrosion could be measured very precisely by inductively coupled plasma atomic emission spectroscopy (ICP–OES). For this, the solutions containing the metal ions were treated with concentrated nitric acid and measured in a simultaneous ICP–OES setup (Spectro Genesis) equipped with a CCD detector system with axial plasma viewing and a special optical-plasma-interface (OPI) system. Due to OPI, matrix effects were reduced dramatically. The CCD camera systems made possible to cover completely the spectral range of 175–775 nm. The optimized Rowland-circle alignment (ORCA) and the Spectro Smart Vision software allowed the measurement and storage of the whole interval of the spectrum (12,000 emission lines). Due to its broad bandwidth (0.362 MHz) and special frequency of operation (f(op) = 27.12 MHz), the plasma remained extremely stable during the measurements.

2.10. Bacterial attachment

Coated and uncoated samples were introduced into a 10-fold diluted, slightly modified VM medium I [60] (ρNaCl = 20 g/L, no thioglycolic acid) inoculated with a 10^8 cells/mL bacterial suspension of *D. alaskensis* AL1, a representative species of corrosion-relevant physiological group of sulfate-reducing bacteria. After 24 h of incubation under anaerobic conditions at 28 °C, the samples were removed, rinsed with sterile, deionised water and stained with 0.36 mM 4′,6-diamidino-2-phenylindole (DAPI) in 1.3 M formaldehyde for 20 min. Care was taken to ensure anaerobic conditions and to avoid contamination of the monoculture, as well as direct sunlight during staining, transportation and storage.

2.11. Cell counting

Fixed and stained cells were counted under an Axio-Imager A1m epifluorescence microscope (Zeiss, Germany) on $1/8 \times 1/8$ mm^2 areas. Data collected on six locations per sample and three parallel samples of each type were averaged.