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Fast and easily applicable glycerol-based spray coating

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ABSTRACT

This work describes the fabrication and evaluation of a transparent hydrogel based spray coating to reduce marine biofouling on glass surfaces. A glycerol based copolymer was synthesized and covalently immobilized by applying a simple spray coating procedure. To test its nonfouling behavior, modified glass surfaces were exposed to different marine fouling species including bacteria, green algae, and blue mussels. For all tested species the coating could considerably reduce the settlement as compared to pristine glass surfaces. The settlement of blue mussels on coated surfaces was additionally compared to polytetrafluoroethylene (PTFE) substrates. The glycerol based copolymer showed an even better resistance against blue mussel adhesion than PTFE. Furthermore, the nonfouling performance of the coating was tested via fibrinogen adsorption after aging coated silica slides under marine conditions. The major aim of this study is to provide an easy synthesis and application procedure for a polyglycerol based nonfouling coating and the evaluation of its nonfouling properties in marine environments.

1. Introduction

Marine biofouling defined as the unwanted settlement and growth of micro- and macroorganisms is of concern to all artificial materials immersed in the ocean, including commercial ships, yachts, monitoring systems, and aquacultures [1–5]. In the case of ships and yachts the main consequence of marine biofouling is an increased hydrodynamic drag of the ship hull which leads to more fuel consumption and thus higher operating expenses and emission of green house gases [6]. Moreover, the biofilm once settled may contribute to microbially induced corrosion or biocorrosion of the substrate material and thus accelerate its aging. In contrast, costs related to biofouling in aquaculture mainly result from material abrasion which necessitates repair or even replacement [6]. The most obvious problem for ocean monitoring systems in contact with seawater is biofouling on optical and electrochemical sensors because the results of measurements may be affected considerably by the presence of films on the sensors [7]. But antifouling protection of the housing is also important, because biofouling can have significant chemical or biological impact on the studied site [4,8].

Since costs due to fouling in commercial shipping exceed the costs in other applications and industries affected by biofouling, research has mainly addressed marine fouling in commercial shipping, where satisfying solutions are already commercially available in terms of fuel savings as well as from an ecological point of view [9,10]. Current strategies to prevent biofouling on ship vessels can be divided into two categories: coatings that release biocides at a specific rate and fouling release coatings (FRCs) that inhibit the settlement of fouling organisms by minimizing the adhesion strength between the surface of the hull and the organisms, thereby facilitating their removal under the hydrodynamic stress caused by the movement of the ship in the water [11]. Concerning biocides, after the ban of tributyl tin (TBT) based compounds, today's biocidal antifouling paints are largely copper based [12]. Commonly, copper is used as cuprous oxide (Cu_2O) which gives commercial ship vessels their typical brownish and reddish color. Despite their considerably reduced toxicity compared to TBT compounds, copper based paints are also subjected to restrictions in several countries [11,13]. In contrast to such active release coatings, passive FRCs which are mainly based on silicone- and fluoropolymers constitute an economically friendly alternative [6]. Since the self-cleaning rate of FRCs depends on physical principles, namely the hydrodynamic stress resulting from the velocity of the vessel in fluid water, early low performing FRCs could only be applied to high speed vessels [11]. According to a model of Schultz and co-workers which relates barnacle adhesion strength to the drag forces generated by the ship

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movement, the best performing silicone coatings still need a vessel speed of at least 10 knots (18.5 km h^{-1}) [14]. The fact that FRCs only work at high vessel speeds is indicated by the estimated figures of their market share by volume, which is around 10% for commercial ships but less than 1% for recreational yachts that spend a large proportion of their time under static conditions [9]. Static conditions also largely prevail in aquaculture and marine monitoring systems. Although FRCs are highly effective in preventing barnacle and mussel adhesion, which are more detrimental in terms of fuel consumption, they generally do not perform well in preventing the formation of a slime layer made of diatoms, smaller algae, and bacteria [15,16].

As antifouling research mainly focuses on technical solutions related to shipping, aquaculture, and ocean monitoring specific solutions are rare [7]. Optical sensors such as beam transmissometer and optical windows, become disrupted by fouling organisms settling on them which makes the pictures blurry or decreases the transmittance of light [17]. As deep sea or coastal oceanographic monitoring systems for monitoring, for example, climate change are generally unmanned, solutions that guarantee a constantly high data quality are needed to enable less expensive and more practical maintenance [18]. Current antifouling systems for optical sensors mainly rely on three distinct approaches [8]: (i) mechanic cleaning using automatized wiping or scrubbing devices, (ii) biocidal release coatings that are comparable to the ones applied in the shipping sector or simple copper plates, and (iii) a controlled generation of biocides using automatic electro-chlorination or acid dispensing devices. FRCs, however, do not play a major role due to the aforementioned fouling release mechanism depending on the vessel speed. Furthermore, they do not sufficiently prevent the settlement of microorganisms such as bacteria and diatoms that preferentially adhere to hydrophobic surfaces [19,20]. The disadvantage for automated scraping and wiping is the mechanical complexity of such devices, and for the use of biocides it is unfavorable that the chemical or biological properties of the studied site may be disturbed by their constant release.

To achieve fouling release properties, even under static conditions, hydrophilic polymers that are commonly applied to render surfaces resistant to proteins or bacteria were tested for their antifouling properties in marine environments [21–25]. Rasmussen and coworkers compared several bulk hydrogels including alginate, agarose, chitosan, and polyvinyl alcohol (PVA) with respect to the adhesion of a marine bacteria species on some macroscopically scaled hydrogels at varying shear rates [23]. The authors could not find any correlation between adhesion and hydrophobicity for the tested polymers. However, PVA exhibited the lowest cell coverage at all shear rates. Liedberg and coworkers [22] prepared optically transparent PEG hydrogel films on glass slides in a two-step procedure via free-radical polymerization of methacrylates under inert gas atmosphere. These coatings showed promising results with respect to their fouling resistance against various microorganisms such as algal zoospores, diatoms, and barnacle cyprids. Hult and coworkers developed thiol-ene hydrogel coatings based on PEG that were applied to glass surfaces with a film applicator and subsequently cured under UV light [24]. The authors demonstrated that protein adsorption as well as adhesion of bacteria and diatoms could be considerably reduced as compared to unmodified glass. We have previously shown that linear methoxylated polyglycerol coatings applied via immersion in a solution of the respective polymer could render microscopic glass surfaces highly protein and cell resistant [26,27]. However, all these approaches which are based on covalently grafting the hydrogel to the glass substrate, have one limitation in common: the application of the coating is laborious and necessitates proper specialist lab equipment. The research we present here was aimed at further developing our linear polyglycerol based coatings to overcome this limitation. In contrast to our previous approach we also change the synthetic route to reduce costs and we further extend our study by including various marine organisms, thus allowing evaluation of the coatings' antifouling properties beyond lab environments in *in vitro* experiments. Therefore, we prepared a silylated glycerol based linear copolymer in a straightforward two-step procedure, which was covalently grafted to planar glass substrates by spraying it under ambient conditions. We tested modified glass surfaces for their ability to resist the adsorption of various marine fouling species and fibrinogen and withstand exposure to marine conditions.

2. Experimental

2.1. Materials

All chemicals and solvents were reagent or HPLC grade, used as received, and purchased from Sigma Aldrich (Steinheim, Germany) unless stated otherwise. Glycidyl methyl ether (GME) was purchased from TCI (Eschborn, Germany), dried over CaH_2 and distilled prior to use. The deionized water used was purified using a Millipore water purification system (MilliQ) with a minimum resistivity of 18.0 MΩ cm. NaCl, NaOH, and aqueous HCl were bought from VWR International (Darmstadt, Germany). Phosphate buffer saline (PBS, 10× concentrated, 90 g/L NaCl, 7.95 g/L Na_2HPO_4, 1.4 g/L KH_2PO_4, pH 7.4) was purchased from Lonza (Cologne, Germany) and was diluted to the final concentration using Milli-Q deionized water. Dialysis was performed in regenerated cellulose tubes from Spectrum laboratories (Spectra/Por® 6 Dialysis membrane, molecular weight cut-off (MWCO) 1000 g mol^{-1} purchased from Roth, Karlsruhe, Germany). Ecospray dispenser was purchased from Roth (Karlsruhe, Germany). Cultures of *Marinobacter hydrocarbonoclasticus* DSM 50418 (*M. hydrocarbonoclasticus*) were purchased from DSMZ (Braunschweig, Germany). Marine broth was purchased from Roth (Karlsruhe, Germany). Blue mussels (*Mytilus edulis*) were collected at the shoreline close to Bremerhaven (Germany) and were further cultivated in a salt and cold water aquarium.

2.2. Methods

^1H and ^{13}C NMR spectra were recorded with a Jeol ECX spectrometer operated at 400 MHz and a Bruker Avance 3 system operated at 700 MHz, respectively, applying analyte solutions at concentrations of 20–100 mg mL^{-1}. The obtained chemical shifts for NMR signals are reported in δ (ppm) values and were referenced to the indicated solvents. Gel permeation chromatography (GPC) measurements were carried out with an Agilent 1100 Series instrument equipped with refractive index detector and polystyrene standards were used for calibration. The GPC measurements were run in using tetrahydrofuran (THF) as eluent (1 mL min^{-1}, 25 °C), and applying three columns in-line, namely Suprema Lux 100, Suprema 1000, and Suprema Lux 3000 (dimensions: 8 nm × 300 nm, particle size: 10 μm, PSS Mainz, Germany). Dissipative quartz crystal microbalance (QCM-D) measurements were performed on a Q-Sense E1 system (Q-Sense AB, Gothenburg, Sweden). SiO_2 coated QCM sensor chips were cleaned with a UV/ozone ProCleaner™ (Bioforce Nanosciences, Ames, IA, USA) equipped with a mercury vapor lamp which generates light with intensity maxima at 254 and 185 nm in the ultraviolet spectral range. A spectrophotometer (Specord 200, Analytik Jena, Germany) was used to determine optical densities.

2.3. Synthesis

Ethoxyethyl glycidyl ether (EEGE) was synthesized according to the literature, dried over CaH_2, and distilled prior to use [28].