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Hydrogel brushes grafted from stainless steel via surface-initiated atom transfer radical polymerization for marine antifouling

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ABSTRACT

Crosslinked hydrogel brushes were grafted from stainless steel (SS) surfaces for marine antifouling. The brushes were prepared by surface-initiated atom transfer radical polymerization (SI-ATRP) of 2-methacryloyloxyethyl phosphorylcholine (MPC) and poly(ethylene glycol) methyl ether methacrylate (PEGMA) respectively with different fractions of crosslinker in the feed. The grafted layers prepared with different thickness were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), ellipsometry and water contact angle measurements. With the increase in the fraction of crosslinker in the feed, the thickness of the grafted layer increased and the surface became smooth. All the brush-coated SS surfaces could effectively reduce the adhesion of bacteria and microalgae and settlement of barnacle cyprids, as compared to the pristine SS surface. The antifouling efficacy of the PEGMA polymer (PPEGMA)-grafted surface was higher than that of the MPC polymer (PMPC)-grafted surfaces. Furthermore, the crosslinked hydrogel brush-grafted surfaces exhibited better fouling resistance than the non-crosslinked polymer brush-grafted surfaces, and the antifouling efficacy increased with the crosslinking density. These hydrogel coatings of low toxicity and excellent anti-adhesive characteristics suggested their useful applications as environmentally friendly antifouling coatings.

1. Introduction

In the marine industry, the accumulation of living organisms such as bacteria, barnacles and algae on artificial surfaces by adhesion, growth and reproduction is known as biofouling [1]. The disadvantageous influences of biofouling include an increase in surface roughness that can significantly reduce the efficiency of boats, and increased ship hull corrosion due to metabolic and other biological processes [2,3].

The severity of biofouling was influenced by many factors [4,5], such as temperature, salinity and voyage speed et al. Nevertheless, these factors cannot be regulated to a large extent. In order to prevent and reduce biofouling, surface modification is an alternative method to alter the surface properties and increase the service life of ship hulls. Therefore, various coatings have been developed in order to chemically inhibit the fouling organisms [6,7].

Tributyltin self-polishing coatings have been the choice for protection of ship hulls in the past. These coatings are usually composed of acrylic polymers with tributyltin groups attached to the polymer backbones, and have proved to be extremely efficient antifouling agents. However, tributyltin compounds have been shown to have deleterious effects upon the environment [8]. An alternative to tin based antifouling coatings has been the utilization of copper antifouling agents. Unfortunately, copper is not an extraordinarily efficient biocide on its own because some of the common marine algae are tolerant to copper [9].

Since tin and copper based coatings are no longer viable choices for protection of surfaces from fouling, research on antifouling coatings has focused instead on non-stick coatings, such as hydrophilic polymer brushes [10,11]. Commonly polymer brush coatings can be covalently grafted by two different approaches, namely "grafting to" and "grafting from" techniques. "Grafting to" approach relies on the chemical bonding of preformed polymers by reacting with functional groups that are present at the surface. Because of steric hindrance of the already attached polymer chains, this method usually suffers the limitation of low grafting density [12,13]. By contrast, the "grafting from" approach is recognized as an effective method to produce polymer chains with high grafting density [14,15]. Due to this attractive feature, the "grafting from" approach becomes the preferred option for the synthesis of thick and stable polymer coatings [16].

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Table 1
Swelling ratio and mesh size of hydrogels.

Sample	SR	Mesh size (nm)
PMPC1	46.2	13.4
PMPC2	35.6	8.74
PPEGMA1	68.5	15.3
PPEGMA2	52.3	9.90

Among various approaches employed to synthesize polymer brushes from a substrate, the surface-initiated atom transfer radical polymerization (SI-ATRP) has been widely used due to the relatively mild polymerization conditions [17,18]. Furthermore, SI-ATRP allows polymerization of many kinds of monomers and becomes a powerful strategy to produce well-defined polymer brushes from various surfaces [19–23].

In the present work, hydrogel brushes were grafted on stainless steel (SS) surfaces by SI-ATRP of 2-methacryloyloxyethyl phosphorylcholine (MPC) and poly(ethylene glycol) methyl ether methacrylate (PEGMA) respectively with different fractions of crosslinker in the feed. Apart from adjustable control of immobilized water fraction, hydrogels could act as a steric barrier for bacteria and large molecules due to their mesh-like structure. In addition, even if highly swollen, hydrogel layers may efficiently screen interactions with the underlying surface [24–26]. The chemical composition and morphology of the modified surfaces were characterized respectively by X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM). The antifouling efficiency of the resulting hydrogel coatings was assayed by bacterial (Pseudomonas sp.) and microalgae (Amphora coffeaeformis) adhesion, and settlement of barnacle (Amphibalanus (=Balanus) amphitrite) cyprids.

2. Materials and methods

2.1. Materials

Stainless steel (SS) foils (AISI type 304) with the thickness of 0.05 mm were purchased from Goodfellow Ltd. of Cambridge, UK. Copper(I) bromide (CuBr), dopamine hydrochloride, poly(ethylene glycol)methyl ether methacrylate (PEGMA, Mn ∼ 475), 2-bromoisobutyryl bromide (BiBB), 2-methacryloyloxyethyl phosphorylcholine (MPC) and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) were purchased from Sigma-Aldrich Chemical Co. A marine Gram-negative bacterial strain of Pseudomonas sp. NCIMB 2021 was obtained from the National Collection of Marine Bacteria, Sussex, U.K.

2.2. Hydrogel synthesis and characterization

Highly swollen hydrogels were prepared using two water-soluble monomers, MPC and PEGMA, and the degree of swelling was varied through the fraction of crosslinker EGDMA. The monomer (MPC or PEGMA, 100.0 mmol), crosslinker (EGDMA, 2.5 or 5.0 mmol), initiator (BiBB, 1.0 mmol) and ligand (PMDETA, 1.0 mmol) were firstly added to the solvent (ethanol, 10 mL). Then the mixture was degassed for 30 min prior to the addition of catalyst (CuBr, 1.0 mmol). The polymerization was carried out at 25 °C for 12 h. The hydrogels prepared at [MPC]([PEGMA]): [EGDMA] molar ratios of 40:1 and 20:1 were denoted respectively as PMPC1 (PPEGMA1) and PMPC2 (PPEGMA2) hydrogels. After polymerization, slabs of a hydrogel were immersed in deionized water for 7 days. Thereafter, the slabs were taken out of solution and quickly blotted with a tissue paper, and the weight W_s was measured. Hereafter, the dry weight W_d was determined after drying at 105 °C for 24 h. Swelling ratio (SR) was calculated as follows:

$$SR = (W_s - W_d)/W_d$$

The characteristic mesh size of the gel was estimated using the following equation [27]:

$$\xi = (C_n n)^{1/2} l v^{-1/3}$$

where C_n was the polymer characteristic ratio (the value 14.6 was used for methyl methacrylate), l = was the sp^3 C—C bond length (1.54 Å), n was the molar ratio of monomer and crosslinker (assuming full conversion), and v was the polymer volume fraction equal to $(S + 1)^{-1}$, assuming the same density for polymer and water.

2.3. Immobilization of initiators for SI-ATRP on SS surfaces

The SS foils were cut into small coupons and cleaned ultrasonically with doubly-distilled water, acetone, and ethanol for 30 min respectively. Then the SS foils were rinsed again with doubly-distilled water and blown dry with argon. Subsequently the SS foils were activated by immersing in the piranha solution (H_2SO_4 (95–97%)/H_2O_2 (30%) = 3/1, v/v) for 60 min to generate a hydroxyl-enriched surface [28], denoted as the SS-OH surface.

For the immobilization of dopamine on SS coupons, dopamine was firstly dissolved in 10 mM Tris-HCl (pH 8.5) with the concentration of 2 mg/mL, and the SS-OH substrates were immersed in the solution for 24 h [29]. Subsequently, the substrates were removed, rinsed with doubly-distilled water, and dried under reduced pressure. Dopamine could self-polymerize to produce a polydopamine (PDA) layer that adsorbed tightly to the substrate. The polydopamine-coated surface was denoted as the SS-PDA surface.

For the introduction of alkyl bromide onto the substrates as the ATRP initiator, the SS-PDA substrate was immersed in 20 mL of dichloromethane containing 2.0 mL of TEA. Then 2.0 mL of 2-bromoisobutyryl bromide in 10 mL of dichloromethane was added dropwise into the reaction mixture at 0 °C. The reaction was allowed to proceed at 25 °C for 24 h [30]. The resulting surface, referred to as the SS-PDA-Br surface, was rinsed three times with a mass of acetone, ethanol, and doubly-distilled water respectively. Finally the resulted substrate was dried under reduced pressure overnight.

2.4. Grafting of non-crosslinked polymer brushes

For the preparation of non-crosslinked MPC polymer (PMPC) or PEGMA polymer (PPEGMA) brushes on the SS-PDA-Br substrate, the surface-initiated ATRP of MPC (PEGMA) was carried out in ethanol (10 mL) solutions at a [MPC]([PEGMA]):[CuBr]:[PMDETA] molar ratio of 100:1:1. The mixture of the monomer (MPC or PEGMA, 100.0 mmol) and PMDETA (1.0 mmol) was degassed for 30 min prior to the addition of CuBr (1.0 mmol). The reaction was allowed to proceed at 25 °C for 12 h to produce the MPC (PEGMA) polymer-grafted (SS-PMPC0 or SS-PPEGMA0) surfaces. After the reaction, the modified surface was washed with ethanol and doubly-distilled water respectively in order to remove the adhered polymer.

2.5. Grafting of crosslinked hydrogel brushes

For the preparation of SS surfaces functionalized with hydrogel brushes, the monomer (MPC or PEGMA, 100.0 mmol), crosslinker (EGDMA, 2.5 or 5.0 mmol) and ligand (PMDETA, 1.0 mmol) were firstly added to the solvent (ethanol, 10 mL) containing the SS-PDA-Br substrate. Then the mixture was degassed for 30 min prior to the addition of catalyst (CuBr, 1.0 mmol). The SI-ATRP was carried out at