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A switchable zwitterionic membrane surface chemistry for biofouling control

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ABSTRACT

This contribution describes a method to minimize biofouling of ultrafiltration membranes by coating the membrane surfaces with a new type of zwitterionic polymer. Poly(2-((2-hydroxy-3-(methacryloyloxy)propyl) dimethylammonio)acetate) (poly(CBOH)) was grafted from polyethersulfone (PES) membranes by UV-photopolymerization. Bacteria deposition studies showed that the poly(CBOH) chemistry performed better than other common anti-fouling chemistries. Biofilm studies showed that poly(CBOH) functionalized PES membranes accumulated half the biovolume as unmodified membranes. A unique feature of this new polymer coating is that it can switch reversibly between the anti-fouling, zwitterion mode and an anti-microbial, quaternary amine mode. Switching pH and time needed for complete switching to occur were evaluated using poly(CBOH) functionalized silicon wafers. Switching pH was determined to be 1.0, with 15 min being required to switch between the zwitterion and quaternary amine chemistries. Biofilm mortality was elevated once the anti-fouling poly(CBOH) zwitterion was switched to the anti-microbial, poly(CB-Ring) quaternary amine, with dead-to-live cell ratio increasing from 0.33 to 1.04.

1. Introduction

Membrane biofouling is a process involving the adsorption of biopolymers, such as glycoproteins and polysaccharides, to the membrane surface; attachment of microorganisms, such as bacteria and algae, to the biopolymer conditioning layer; and eventually growth of the microorganisms into a fully developed biofilm on the membrane surface [1]. Biofouling is a major hindrance to membrane usage, because unlike other types of fouling, microorganisms can grow, multiply, and relocate on a membrane [2,3]. Biofouling causes a transient flux decline in the case of constant-pressure filtration or a pressure increase in the case of constant flux filtration, either of which increases the process operational costs [4]. Chemical cleaning is required for fouled membranes, which leads to process downtime and shortens the membrane lifetime [5].

Biofouling prevention not surprisingly has been a trending topic in the literature. Surface modification of membrane surfaces has been the most common approach to reducing biofouling, and typically is done by chemical treatments or coatings [6–9]. Anti-fouling coatings make the membrane surface less favorable for biopolymer/bacteria attachment by following the "Whitesides' rules": making the surface more hydrophilic, including hydrogen-bond acceptors, excluding hydrogen-bond donors, and having an overall neutral electrical charge [10,11]. Commonly studied anti-fouling coatings include poly(ethylene glycol) (PEG) [12,13] and zwitterions such as carboxybetaine [14,15], sulfobetaine [16,17], and phosphobetaine [18,19], which are net charge neutral molecules that contain positive and negative charge groups. These coating types can form a strong hydration layer that decreases

Abbreviations: a.u., absorbance units; AIBN, azobisisobutyronitrile; AFM, atomic force microscopy; ATR-FTIR, attenuated total reflectance Fourier-transform infrared spectroscopy; ATRP, atom transfer radical polymerization; BP, benzophenone; BPA, 2-bromo-2-methylpropionic acid; BPY, 2,2′-bipyridyl; CBOH, 2-((2-hydroxy-3-(methacryloyloxy)propyl)dimethylammonio)acetate; CB-Ring, 2-(methacryloyloxymethyl)-4,4-dimethyl-6-oxomorpholin-4-ium; CBtBu, N-(2-tert-butoxy-2-oxoethyl)-2-hydroxy-3-(methacryloyloxy)-N,N-dimethylpropan-1-aminium iodide; CLSM, confocal laser scanning microscopy; DCM, dichloromethane; DMF, N,N-dimethylformamide; FTIR, Fourier-transform infrared spectroscopy; GFP, green fluorescent protein; GMA, glycidyl methacrylate; GPC, gel permeation chromatography; HMDS, hexamethyldisilazane; LB, Luria-Bertani; MBAA, N,N′-methylenebis(acrylamide); PDMAB, poly(4-[dimethyl(2′-methacryloyloxyethyl)ammonio]butanoate); PEG, poly(ethylene glycol); PEGMA, poly(ethylene glycol) methacrylate; PES, polyethersulfone; PMAPS, poly(3-[dimethyl(2′-methacryloyloxyethyl)ammonio]propanesulfonate); PMPC, poly(2-(methacryloyloxy)ethyl phophorylcholine); SEM, scanning electron microscopy; SFE, surface free energy; SPE, [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide; THF, tetrahydrofuran; TFA, trifluoroacetic acid

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biofoulant adsorption or attachment [12,20]. Recently, we showed that membrane biofouling resistance can be enhanced by combining chemical surface modification with physical surface modification using a nano-scale line and groove pattern [21].

Application of anti-microbial agents or biocides is another common strategy used to control membrane biofouling by killing bacteria that attach to the surface. Quaternary amine containing coatings are thought to disrupt the cell membrane, resulting in cell leakage and eventually cell death [22,23]. Carbon nanotubes and graphene oxide have been shown to deactivate the bacteria upon contact with the membrane surface [24,25]. Silver nanoparticles that severely damage the bacteria cell membrane also have been incorporated in membranes [26,27].

There have been attempts to combine anti-fouling and anti-microbial approaches on one membrane [28]. One strategy has been to use an anti-fouling chemistry combined with silver nanoparticles [29–31]. A second strategy has been to add two chemistries to the membrane surface, one anti-fouling and the other anti-microbial [32–37]. One such method is to pattern the two chemistries on the membrane in alternating rows of a stimuli-responsive polymer and a biocide, such that foulants will be brought in contact with the biocide, killed, and released by the stimuli responsive polymer [33].

This paper contributes a method for applying one chemistry to a membrane surface that is capable of switching between a unique anti-fouling, carboxybetaine zwitterion mode and an anti-microbial, quaternary amine mode [38,39]. The novelty of this chemistry is that it can switch between the anti-fouling and the anti-microbial mode by changing the environment pH. Similar zwitterion chemistries with switching capabilities have been studied as hydrogels [40,41]. This study is the first to apply a switchable zwitterion chemistry to control membrane biofouling, and the first to study its effectiveness under long-term exposure to water. Polyethersulfone ultrafiltration membranes were modified with this chemistry and other anti-fouling chemistries to provide direct comparisons of the resistance to bacteria attachment, cell viability, and biofilm growth on the membrane surfaces.

2. Materials and methods

2.1. Materials

All chemicals were used as received, unless otherwise noted. The following chemicals were purchased from Sigma Aldrich: sarcosine *tert*-butyl ester hydrochloride (97%), glycidyl methacrylate (GMA, 97%), zinc tetrafluoroborate hydrate, iodomethane (99%), trifluoroacetic acid (TFA, 99 + %), Amberlite® IRA-400 chloride form, N,N-dimethylformamide (DMF, anhydrous, 99.8%), [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (SPE, 97%), benzophenone (BP, 99%), N,N′-methylenebis(acrylamide) (MBAA, 99%), poly(ethylene glycol) methacrylate (PEGMA, M_n = 360 g/mol), 2-bromo-2-methylpropionic acid (BPA, 98%), copper(I) bromide (99.999%), 2,2′-bipyridyl (BPY, 99 + %), chloroform-d (99.8%), deuterium oxide (99.9%), trifluoroacetic acid-d (99.5%), azobisisobutyronitrile (AIBN, 98%), hydrogen peroxide (30% in water), and sulfuric acid (95–98%). The following chemicals were purchased from Acros Organics: chloroform (99%), dichloromethane (DCM, pure), diethyl ether (99.5%), and diiodomethane (99 + %). Acetone (99.5 + %), ethanol (99.5% anhydrous), sodium bicarbonate (99 + %), tetrahydrofuran (THF, 99 + %), and acetonitrile (anhydrous, 99.9%) were purchased from Fisher Scientific. Sodium hydroxide (97 + %) was purchased from Alfa Aesar. Aqueous solutions were made with deionized water from a Milli-Q water purification system (Millipore-Sigma).

Prior to reaction, GMA was passed through a column of inhibitor remover (Sigma Aldrich) to remove monomethyl ether hydroquinone. Anhydrous DMF was opened and was stored in a nitrogen atmosphere glovebox (MBraun USA). Poly(glycidyl methacrylate) (PGMA, MW = 290,000 g/mol, PDI = 1.7 (GPC)) [42] used for dip-coating silicon wafers was prepared by radical polymerization of GMA in methyl ethyl ketone at 60 °C using AIBN as initiator. Amberlite® IRA-400 chloride form was converted to hydroxide form by reacting with a 1 M sodium hydroxide aqueous solution using a 1 meq resin:2 mmol sodium hydroxide stoichiometry for 35 min.

PES ultrafiltration membranes were kindly received from Microdyn-Nadir GmbH (PM UP150, Microdyn-Nadir, 150 kDa MWCO) and GE Water & Process Technologies (GE Osmonics, unknown MWCO). The GE PES membrane was a gift from GE. Polished silicon wafers (1 cm × 3 cm) were purchased from Nova Electronic Materials.

The synthesis of the carboxybetaine zwitterion monomer (CBOH) is presented in Supporting information in two parts: (1) synthesis of the protected monomer (CBtBu) and (2) deprotection to yield the final product. The steps are similar to those reported by Cao et al. [38], but with modifications. Experimental details (Fig. S3) and ^{1}H- and ^{13}C NMR spectra (Figs. S4 and S5) are given in the Supporting information.

2.2. Surface modification

2.2.1. UV polymerization

UV polymerization was performed to graft poly(CBOH), poly(PEGMA), and poly(SPE) from PES ultrafiltration membranes. Fig. S2 in the Supporting information depicts the process for polymerizing poly(CBOH) from PES membranes. PES membranes were rinsed in deionized water to remove pore filler and pat dried. Photo-initiator, BP, was entrapped in PES membranes by immersing the PES membranes in a solution of 100 mM BP in acetonitrile for 4 h with stirring. Acetonitrile was chosen because it swelled but did not dissolve the PES. The PES membranes were rinsed thoroughly with deionized water to collapse the swollen PES to entrap the BP and then pat dried. Next, UV polymerization was performed using a 365 nm UV light from an EL series UVLS-28 UV lamp (UVP, VWR International) (Husson lab) or a 315–600 nm range UV lamp (UVACUBE100 curing chamber equipped with Dr. Hönle lamp UV 150 F and filter H1 (Hönle UV technology)) (Freger lab).

Modification of Microdyn-Nadir PM UP150 PES membranes by poly(CBOH) and poly(SPE) was done in the Husson lab at Clemson University. The reaction solution comprised 1 M CBOH or SPE and 0.01 M MBAA in deionized water. A piece of BP-entrapped PES membrane was placed in a 50 mL glass beaker and 0.17 mL of reaction solution/cm^2 membrane area was placed on the membrane active side. A 30 mL glass beaker was placed on top of the membrane and the reaction solution such that no air bubbles were present between the membrane and the top glass beaker. For flux experiments, a glass petri-dish was used instead of beakers, with the membrane being placed in the top cover of petri-dish and the bottom part used to form the thin film of reaction solution. The membrane was exposed to 365 nm UV light with an intensity of at least 500 μW/cm^2 for 4.5 h (CBOH) or 25 min (SPE) from a source placed approximately 6.5 cm above the membrane. Modified membranes were rinsed thoroughly with deionized water, placed in deionized water in a shaker bath overnight (> 15 h), and then pat dried. Samples for ATR-FTIR were vacuum dried at 20–25 °C and −0.78 to −0.95 barg. Samples for biofilm studies were immersed in a 15 wt% aqueous glycerol solution and dried in air for shipment to the Herzberg lab at Ben Gurion University.

Modification of GE Osmonics PES membranes was done in the Freger lab at Technion. The following protocol was used for poly(CBOH), poly(SPE), and poly(PEGMA) UV polymerizations. First, BP was entrapped in PES membrane samples as described earlier in this section. Then a piece of the membrane was placed in the cover of a glass Petri dish, 5 mL of a monomer/cross-linker solution in DI water (0.5 M monomer, 0.005 M MBAA) was put on top of the membrane, and the bottom part of the Petri dish turned upside down was placed on the membrane. This procedure produces a thin layer of the modification solution on top of the membrane between the two glass Petri dish components. The assembly was placed in the UV chamber (UVACUBE