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Random copolymer films as potential antifouling coatings for reverse osmosis membranes

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ABSTRACT

Adsorption of biopolymers such as proteins and polysaccharides is known to expedite/facilitate microbial attachment and subsequent formation of biofilm on membrane surface that ultimately results in membrane biofouling. Therefore, surfaces that resist the adhesion of biopolymers can potentially block the irreversible attachment of microorganisms as well. Recently, it was shown that random copolymerization of the hydrophilic hydroxyethylmethacrylate (HEMA) monomer with the hydrophobic perfluorodecylacrylate (PFA) monomer leads to a surface that interferes with the adsorption of a representative protein, bovine serum albumin (BSA). In this work, we explore the feasibility of using these copolymer films as potential antifouling coatings on commercial RO membranes. The films were deposited using iCVD technique that allows good composition control, is solvent-free and can be done readily at room temperature. Characterization and performance evaluation of the coated membranes was carried out using different techniques. Scanning Electron Microscopy images showed the coatings to be conformal and continuous. The surface topology of the membranes was analyzed with Atomic Force Microscopy. The results confirmed that the copolymer film does not cause a significant increase in the membrane surface roughness (a crucial parameter in biofouling). Short-term permeation tests with DI water proved that copolymer films of 20 nm thickness did not cause any significant decline in permeate water flux.

Keywords: RO membranes; Surface modification; Initiated chemical vapor deposition; Biofouling resistant coatings; Permeation; Hydrophilicity

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1. Introduction

Reverse osmosis membranes are presently being used in a wide range of applications, including brackish/seawater desalination, drinking water treatment, and wastewater reclamation. A major obstacle for the efficient application of this process is fouling by micro-organisms [1]. Biofouling has been called the Achilles heel of membrane processes because unlike other types of fouling, it cannot be eliminated by pretreatment of feed water [2]. Therefore, membrane biofouling has been found to occur extensively on RO membranes even after significant pretreatment of the influent stream [3]. The most notable deleterious consequences of biofouling include long-term permeate flux decline and increase in salt passage [4].

Primary adhesion of micro-organisms is a critical early stage event in the overall process of biofouling and largely controlled by physicochemical factors such

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as hydrodynamics, solution chemistry, and interfacial forces [5]. Once deposited and attached, cell grow, multiply and produce extra-cellular polymers (EPS), which form a tangled matrix of fibers that provide structure to the assemblage termed a "biofilm". Once formed, a biofilm is difficult to remove because the EPS layer strongly adheres cells to the membrane surface and protects microbes from attack by predators and biocides.

Prior to bacterial adhesion, the membrane surface is covered with a so-called conditioning film consisting of macromolecules, such as humic substances, polysaccharides and proteins, which are present in trace amounts in water [6]. On the other hand, bacterial cell surfaces are composed of a complex mixture of proteins, phospholipids, polysaccharides, lipopolysaccharides (LPS), and other biopolymers [7]. The biopolymers adsorbed on the membrane surface can subsequently recruit cells or micro-organisms to the surface that will eventually cause biofouling. Hence, surfaces that resist adhesion/adsorption of these macromolecules can potentially block other foulants as well [8].

Recently, Gleason and coworkers [9] copolymerized the hydrophilic hydroxyethylmethacrylate (HEMA) with the hydrophobic perfluorodecylacrylate (PFA) using initiated chemical vapor deposition (iCVD) technique to create a randomly amphiphilic thin polymer film. They also studied the adsorption of a representative protein, Bovine Serum Albumin (BSA) on these films using quartz crystal microscopy with dissipation monitoring (QCM-D). Proteins adsorbed on to these copolymer films less readily than on to either of the respective homopolymers, indicating a synergistic effect resulting from the random copolymer presenting molecular-scale compositional heterogeneity. The adsorption was minimum at intermediate copolymer chemistry (~40% PFA).

Encouraged by the above findings, it was decided to explore the feasibility of using these copolymer films as potential antifouling coatings on commercial RO membranes. Ultra-thin (~20 nm) films of the HEMA-PFA copolymer were deposited on membranes from different manufacturers using the iCVD technique. The coated membranes were then characterized by various techniques: AFM was used to measure the surface roughness, SEM for surface morphology, and contact angle (CA) for hydrophilicity. Short-term permeation tests were performed with DI water and 0.2 molar NaCl solution using a lab-scale cross flow permeation cell.

2. Experimental

2.1. Thin film deposition

The depositions were performed in a disc-shaped reactor (Fig. 1) with a diameter of around 50 cm and a depth of 10 cm. An array of Chromalloy filaments is present inside approx. 2 cm above the reactor surface. The two monomers, HEMA and PFA, were heated in separate crucibles to 80°C and 70°C, respectively and then transported to the reactor using needle valves. The initiator for the polymerization reaction terbutylperoctoate (TBPO), and nitrogen are fed separately through mass flow controllers (MKS, 1152). Heating of the filaments results in the thermal decomposition of the initiator molecules and hence the commencement of the copolymerization. The sample stage is back-cooled using a chiller/heater (NESLAB) and the substrate temperature is adjusted to prevent heating from the filaments [10].

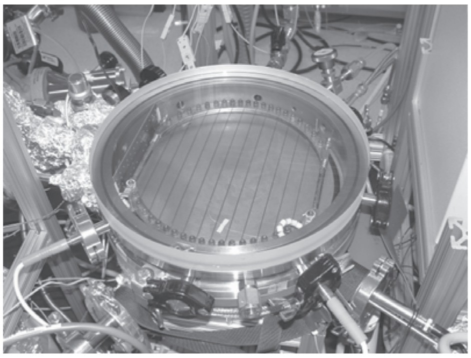

Fig. 1. Picture of the iCVD reactor used for the copolymer film depositions.

The chemical composition of the deposited films can be controlled by adjusting the flow rates of monomers keeping the overall flow rate constant. In our case, the flow rate of PFA was varied while keeping the HEMA flow rate constant. Copolymer films with the following compositions were deposited: 0, 10, 40, 75 & 100% PFA. Nitrogen patch flow is used to keep the total flow rate constant so that the residence time in the reactor does not vary. All the experiments were performed at a pressure of 200 mTorr and the filament and stage temperatures were maintained at 210°C and 30°C, respectively.

The film thickness was monitored real-time by reflecting a He-Ne laser (JDS Uniphase) off a Si wafer placed next to the membrane and recording the interference laser signal intensity as a function of time. The final film thickness on Si was measured after the deposition using variable angle spectroscopy ellipsometry (VASE, JA Woollam M-2000) at three different angles (65, 70 and 75 degrees) with the wavelength range of 315 nm to 700 nm. The data is fit using a Cauchy-Urbach model. The real-time monitoring of the film thickness on the membrane using a Si wafer relies on the fact that the deposition rates on the Si wafer and on the RO membranes are similar.

2.2. AFM Characterization

Atomic force microscopy (AFM) was used for direct analysis of membrane surface roughness. A large number of recent studies have shown that surface roughness is an important factor in determining the rate and extent of membrane fouling [11,12]. The AFM observations were performed on a multimode Nanoscope V5 from Veeco Instruments, Inc. in tapping mode with silicon nitride cantilevers. Measurements were done at 5 different locations for each sample and the average value calculated.

2.3. Contact angle measurements

The basis contact angle measurement is related to the three-phase equilibrium that occurs at the contact point of the solid/liquid/vapor or solid/liquid/liquid interface. In our case, where the phases are membrane/water/air, the contact angle is a measure of wettability of the membrane, i.e., the capacity of water to be adsorbed on the membrane. This can be interpreted as the hydrophobicity/hydrophilicity of the membrane. The sessile drop method was used in our research. This method, also called the water droplet method, is based on measuring the contact angle between a water droplet and the membrane surface using a goniometer.

Square pieces (1 cm × 1 cm) of the membrane were cut and attached to glass slides using double-sided tape. A droplet of DI water (20 μl) was carefully placed on the membrane with a micropipette. A light source was placed behind the sample and the light was focused through a slit. The contact angle was measured with the goniometer. This procedure was repeated for 5 different locations on each sample.

2.4. SEM Characterization

The surfaces of both bare and coated membranes were examined using a scanning electron microscope (SEM, JEOL JSM-6400) at 15–20 kV to study the surface morphology and coating thickness. In order to make them conductive, the samples were coated with an ultra-thin (5–10 nm) layer of gold prior to examination with FESEM at very high magnifications. However, due to difficulty in obtaining decent images caused by charging of the samples, it was decided to continue the characterization with environmental scanning electron microscopy (ESEM).

2.5. Permeation tests

Short-term permeation tests of the membranes were carried out with a commercial cross-flow membrane filtration unit (Sepa CF 042, Sterlitech Corporation, USA). The feed pressure was maintained around 700 psi using a pressure control valve and a secondary metered valve. The temperature of the feed was maintained around 25°C using a NESLAB chiller. The permeate was collected in a 50 ml measuring cylinder and the time recorded with a stopwatch. In order to measure the salt concentration of the permeate, a conductivity meter, CDH-152, from Omega Engineering, Inc. was used.

3. Results and discussion

Representative AFM images of TFC-HR membranes from KOCH Membrane Systems, Inc. coated with copolymer films of different chemistries are shown below (Fig. 2). There is a slight increase in the surface roughness with increasing hydrophobic PFA content, which is in agreement with the results reported by Baxamusa et al. [9]. Nevertheless, the average roughness for all three coated membranes with different coating compositions are not very different from the bare (uncoated) membranes.

Similar surface roughness results were observed for SG-RO membranes from GE Osmonics, Inc. where the average surface roughness of both the bare and coated membranes was noted to range between 10–15 nm (Fig. 3).

Scanning electron microscopy images of TFC-HR membranes are shown below (Fig. 4). In one of the coated specimens, the copolymer film was deliberately scratched

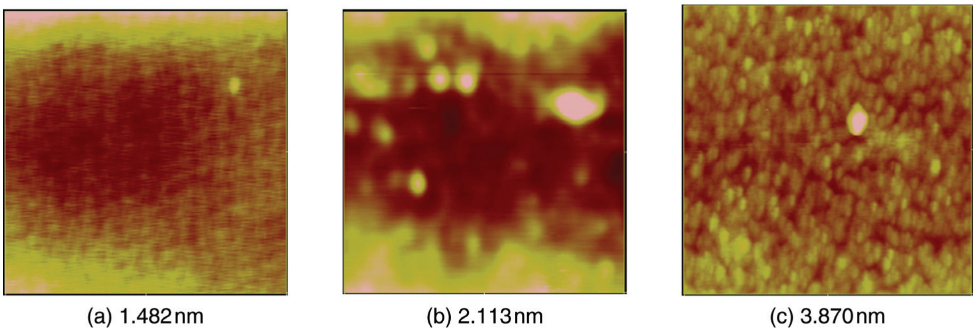
(a) 1.482 nm (b) 2.113 nm (c) 3.870 nm

Fig. 2. AFM images and the rms roughness values of KOCH membranes coated with (a) 10% (b) 40% (c) 75% PFA.

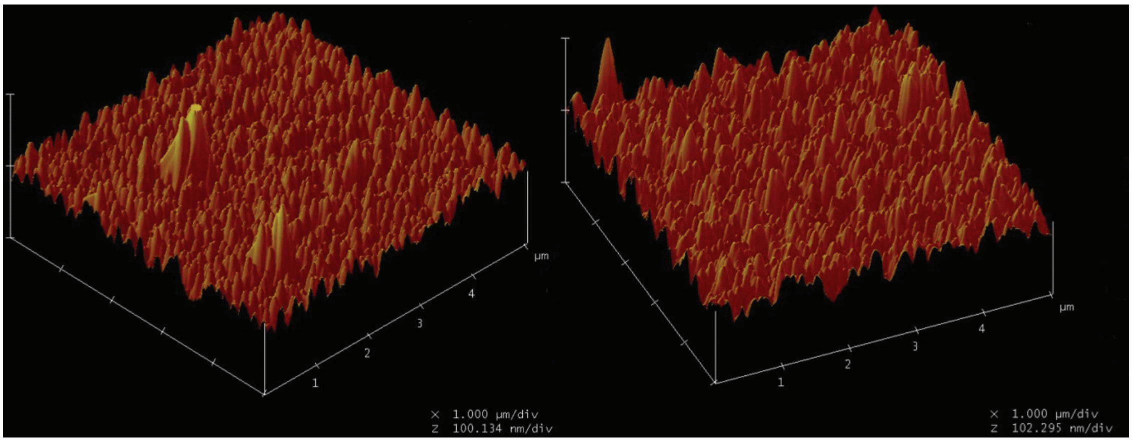

Fig. 3. Surface topology images for SG membranes (a) bare (b) coated with 40% PFA. Note that the X and Y dimensions are both 5 µm (1 µm/division), while the Z-scale is 200 nm (100 nm/division).

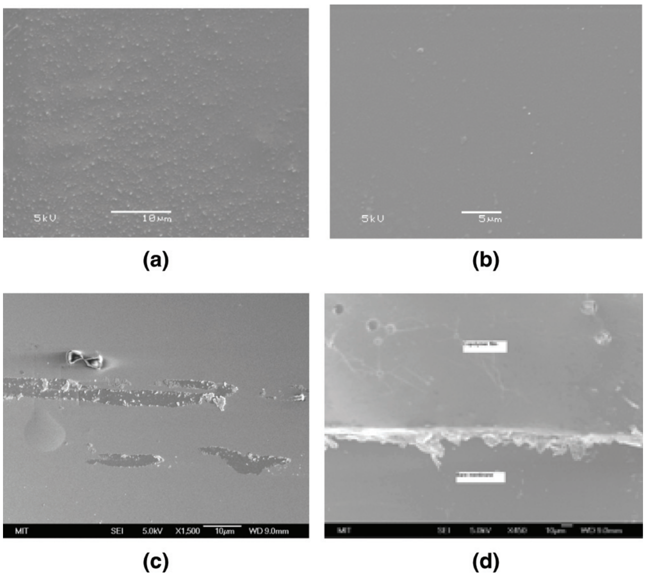

Fig. 4. SEM images of TFC-HR membranes (a) without coating, (b) with a complete coating, (c) with coating scratched from some areas, and (d) coated and bare portions side by side.

from some areas to show the difference between the original membrane surface and the coated surface (Fig. 4c). In yet another sample, some portions of the membrane were left uncoated to observe the bare and coated regions next to each other (Fig. 4d). Altogether, these images provide a strong evidence of the conformality and uniformity of the HEMA-PFA copolymer films deposited by the iCVD method.

Hydrophilicity/hydrophobicity of membrane surfaces is an important property in water filtration processes such as reverse osmosis. In addition to affecting the permeate water flux, it also plays a crucial role in membrane biofouling, with attachment being generally more favorable with hydrophobic, non-polar surfaces. [13]. Therefore, it is usually preferred to use a membrane which has a relatively hydrophilic surface.

The composite images shown in Fig. 5 reveal the relative degree of hydrophilicity of different membrane surfaces. Among the bare membranes, SWC1 (Hydranautics, Inc.) is the most hydrophilic with an average contact angle of ~25° while TF-RO-SG (GE Osmonics, Inc.) is the least hydrophilic with an average angle of ~50°. The copolymer film with the intermediate composition i.e., 40% PFA, is somewhat hydrophobic with an average contact angle of ~52°.

In order to determine the effect of coating on the permeation characteristics of the mambranes, short-term permeation tests with DI water were carried out. The following bare and coated membranes were: SWC1 (Hydranautics), TF-RO-SG (GE Osmonics, Inc.), and TFC-HR (Koch Membrane Systems, Inc.). All coated membranes contained Copolymer films of identical thickness (20 nm) and ~40% PFA content. The permeate flux was determined by recording the time taken to collect a given volume of permeate in a measuring cylinder. The results are plotted as a bar chart as shown in the Fig. 6.

Since the HEMA-PFA copolymer is not as permeable to water molecules as the polyamide active layer on top of the RO membrane, it is natural to expect a decrease in water permeability of the membrane after the deposition

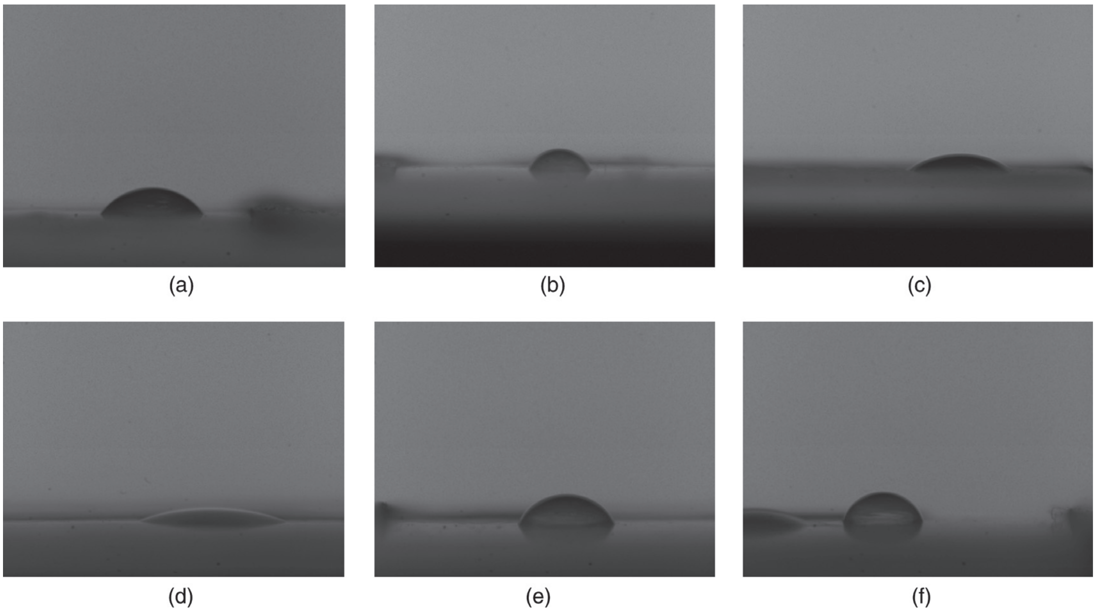

Fig. 5. Image of water droplets formed on bare membrane surfaces (a) TFC-HR (b) TF-RO-SG, and (c) SWC1; and coated surfaces of different copolymer compositions (d) 10% PFA, (e) 40% PFA, and (f) 75% PFA.

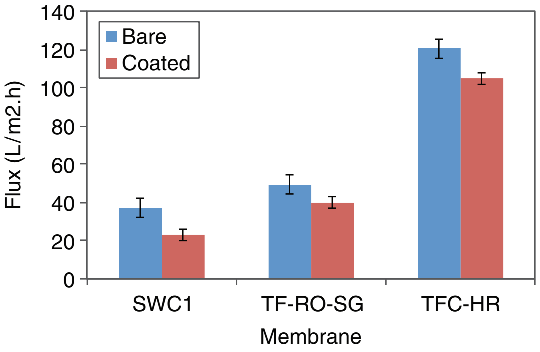

Fig. 6. DI water flux for different commercial membranes with and without copolymer film.

of a thin film of the copolymer. The percentage decline in permeate water flux are as follows: 38% (SWC1), 23% (TF-RO-SG), and 13% (TFC-HR). The membrane least affected by the presence of the coating is TFC-HR from Koch membrane systems, Inc.

4. Conclusions

In this work we have shown that HEMA/PFA copolymer thin films can be coated on the commercial RO membranes using iCVD without any damage to the membrane surface. 20 nm coatings with 40% PFA content does not alter the surface roughness and hydrophilicity characteristics of the RO membranes. The copolymer coating resulted in the decline of permeate flux with the TFC-HR membrane from KOCH showing the lowest effect of 13% flux decline.

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