Surface nano-structuring of reverse osmosis membranes via atmospheric pressure plasma-induced graft polymerization for reduction of mineral scaling propensity

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ABSTRACT

Surface nano-structuring of polyamide desalination membrane with a hydrophilic poly(methacrylic acid) was shown to reduce the membrane mineral scaling propensity as demonstrated with calcium sulfate dihydrate (gypsum). A two-step approach was employed, whereby the active polyamide (PA) layer of a thin-film composite (TFC) synthesized membrane was activated with impinging atmospheric plasma, followed by a solution free-radical graft polymerization (FRGP) of a water soluble methacrylic acid (MAA) monomer, at 60 °C and initial monomer concentration of 5–20% (v/v), onto the surface of the PA-TFC membrane. The approach of creating a layer of end-grafted poly(methacrylic acid) (PMAA) surface chains was first developed and evaluated using a surrogate polyamide membrane layer interfacially polymerized onto a thin poly(ethyleneimine) (PEI) film coated onto a silicon wafer. The resulting PMAA–PA-PEI–Si surrogate membrane surface was hydrophilic with a water contact angle range of 10–17°. Structuring of the PA-TFC membrane at equivalent FRGP reaction conditions resulted in membranes of higher permeability (by a factor of 1.3–2.26) relative to a commercial RO membrane of a similar surface roughness (∼70 nm) and salt rejection. Flux tests of membrane mineral scaling demonstrated that membrane mineral scaling propensity can be measurably reduced, relative to commercial membrane of the same salt rejection, while yielding equivalent or higher water permeability. The onset time for gypsum scaling for the optimal membrane surface (prepared at 10% (v/v) initial MAA concentration) was retarded by a factor of 2–5 relative to the commercial RO membrane. Current work is ongoing to further optimize the surface structure in order to increasing scaling resistance and assess the impact of surface structuring on nucleation of mineral salt crystals.

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1. Introduction

Mineral salt scaling of polyamide thin-film composite (TFC) reverse osmosis (RO) and nanofiltration (NF) membranes is a major impediment to achieving high product water recovery when desalting brackish water [1–3]. Mineral salt scaling occurs when mineral salt ions concentrate near the membrane surface, leading to solution supersaturation and subsequently salt crystallization at the membrane–solution interface [4–8]. Surface scaling results in both permeate flux decline and potential membrane damage. It is known that the membrane surface topography and chemistry have a direct impact on membrane fouling (e.g., colloidal and biofouling) [9,10]. Recently, surface graft polymerization of RO/NF membranes with hydrophilic polymers has been proposed as a means of retarding biofouling in saccharose ($M_w = 342$, 5.5 g/l) solutions [11,12] and reducing protein (BSA at pH 4.8) adhesion [13] via modification of the native substrate surface chemistry and topographical surface structure. The end-grafted polymer chains have significant mobility when exposed to a good solvent. Therefore, it is reasonable to expect that these protective polymer layers can reduce the propensity of foulants from adhering to the membrane surface as reported in numerous studies [14–18]. The possible benefit of membrane surface structuring with end-grafted hydrophilic polymer chains to reduce membrane mineral scaling propensity has not been previously explored.

Mineral scaling on membrane surfaces is a process that results from the deposition of nuclei and bulk formed crystals onto the membrane surface or direct nucleation onto the membrane surface, and subsequent crystal growth by a diffusion-reaction mechanisms [8,19]. The hypothesis of the present approach is that a sufficiently dense coverage by terminally anchored hydrophilic water soluble polymer chains on the active (polyamide) layer of the RO/NF membrane surface should reduce the membrane-scaling propensity under super-saturated solution conditions. Such reduction in

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scaling propensity could possibly be due to a reduction of the rate of nucleation and/or adhesion of mineral crystals to the surface. Also, the water soluble polymer graft layered could be beneficial to maintain the water permeability of the RO/NF membrane provided that the structure structuring does not result in surface blockage. The above strategy was demonstrated in the current study, with respect to mineral scaling by calcium sulfate dihydrate (gypsum) which is often encountered in inland water brackish water desalination, via nano-structuring RO/NF membranes by atmospheric pressure plasma-induced free-radical graft polymerization (APPI-FRGP).

In the present work, the end-grafted polymer layer was formed on a low pressure polyamide membrane by a recently developed two-step process of solution graft polymerization of a water soluble monomer onto active surface sites created by treatment with an impinging atmospheric pressure plasma source [20,21]. The atmospheric plasma mixture, followed by surface oxygenation results in the formation of peroxides of surface density that can be adjusted by the plasma source power, exposure period, distance between the substrate and the plasma source, as well as the gas mixture used for the plasma source [20]. In the present work, methacrylic acid, reported in previous studies as an effective membrane antifouling surface modifier [18], was selected as the monomer of choice to develop the nano-structured polyamide RO membrane surface with end-grafted poly(methacrylic acid) (or PMAA) chains. The resulting membranes were then evaluated with respect to their gypsum scaling propensity and general performance.

2. Experimental

2.1. Materials and reagents

Interfacial polymerization to create the active polyamide layer was accomplished using 1,3-phenylenediamine (MPDA, ≥99%) and 1,3,5-benzenetricarboxylic chloride (TMC, 98%), purchased from Sigma–Aldrich (St. Louis, MO). Ultra-pure deionized water was produced by filtering distilled water through a Milli-Q filtration system (Millipore Corp., Milford, MA), and ESPA1 (Hydranautics, Oceanside, CA). The ESNA1-LF, ESPA1, TFC-ULP and LFC1 membranes had surface roughness of 55 [22], 123 [17], 42 [23] and 73 nm, respectively, salt rejection of 93% [24], 96% [17], 99% [23], and 95%, respectively, and water permeability of 0.21 × 10⁻¹⁰ m/s Pa [22], 0.13 × 10⁻¹⁰ m/s Pa [25], 0.18 × 10⁻¹⁰ m/s Pa [23], and 1.5 × 10⁻¹⁰ m/s Pa, respectively.

2.2. Preparation of polyamide membrane surfaces

Polyamide–poly(ethyleneimine)–silicon (PA-PEI–Si) membrane test surfaces were prepared with a typical loose RO membrane PA surface chemistry but with low surface roughness to assess the effect of graft polymerization on surface topography. The PA–PEI–Si surfaces were first used to determine the reaction conditions suitable for surface nano-structuring, as well as to evaluate the thickness of the grafted polymer layer. The PA–PEI–Si test surfaces were prepared by creating a relatively smooth thin PA layer interfacially polymerized onto a PEI-Silicon (PEI-Si) substrate (~7 nm PEI film thickness), followed by methacrylic acid graft polymerization onto the PA surface.

The wafer samples were first cleaned in an acid-etching process with a mixture of 70:30 sulfuric acid to hydrogen peroxide for 10 min at 90 °C and then triple rinsed to remove residuals and oven dried (caution: this piranha solution reacts violently with many organic materials and should be handled with extreme care). About 1 mL of a 0.3 wt% aqueous solution of PEI was used to assist in the adhesion of PEI to the silicon wafer sample, which was then spin-coated (using spin-coater model PWSM32, Headway Research Inc., Garland, TX) on the cleaned silicon surface at 2500 RPM for 30 s in an inert nitrogen environment. About 1 mL of a 2.5 wt% aqueous solution of MPDA was then applied by spin-coating at 2500 RPM for 30 s onto the PEI–Si surface. Once the formation of the MPDA–PEI–Si silicon surface was accomplished, approximately 1 mL of a 0.13 wt% TMC solution was dispensed (via a syringe) onto the surface to initiate polyamide interfacial polymerization at a controlled chamber temperature of 25 °C. The reaction was allowed to proceed for approximately 2 min, at which time the surface was washed with DI water to remove unreacted monomer and the PA–PEI–Si surface was vacuum-oxygen dried at 80 °C for a period of 0.5 h. The PA–PEI–Si surfaces were subsequently nano-structured by graft polymerization as described in Section 2.3.

Poly(methacrylic acid) surface nano-structured PA-TFC (SNPA-TFC) membranes, evaluated with respect to their mineral scaling propensity, were prepared by first synthesizing an active PA layer on a polysulfone (PSF) support via conventional polyamide interfacial polymerization technology [26]. Briefly, the PSF support membrane was dipped into an aqueous solution containing MPDA (2.5%, w/w) for 3 min, followed by draining of the excess solution. Subsequently, the membrane was dipped into the organic phase containing TMC (0.13%, w/w) in hexane and allowed to react for ~20 s, followed by draining the excess organic solution and oven curing at 80 °C for 30 s. The membrane was then rinsed with DI water and stored in a 1% aqueous NaHSO3 solution. The resulting PA-TFC membrane had nanofiltration membrane performance with a water permeability of 5.2 × 10⁻¹⁰ (m/s Pa) and 30% NaCl salt rejection measured at 1000 ppm.

2.3. Poly(methacrylic acid) surface nano-structured PA membrane surfaces

Two different sets of poly(methacrylic acid) surface nano-structured polyamide membranes were prepared. The first was a membrane test surface prepared by using the surrogate PA–PEI–Si surfaces (Section 2.2). The second set was prepared using the PA-TFC membrane synthesized to match the desired permeability for the subsequent graft polymerization step.
The PA-PEI–Si substrates and the PA-TFC membranes (SNS-PA-PEI–Si and SNS-PA-TFC, respectively) were surface activated by atmospheric pressure plasma followed by graft polymerization. Briefly, an impinging atmospheric pressure plasma source (produced using a mixture of 1 vol% of ultra-high purity hydrogen (99.999%) in helium (99.999%)) was used to activate the PA-PEI–Si and the PA-TFC membrane for a period of ∼10 s at RF power of 10–60 W. It is noted that, for the above plasma treatment conditions, the permeability and salt rejection of the surface plasma treated PA-TFC membrane (Section 2.2) did not change as a result of the plasma treatment process. Following plasma surface exposure, the substrates were exposed to ultra-high purity oxygen for 10–60 W. It is noted that, for the above plasma treatment conditions, the permeability and salt rejection of the surface plasma treated PA-TFC membrane (Section 2.2) did not change as a result of the plasma treatment process. Following plasma surface exposure, the substrates were exposed to ultra-high purity oxygen for a period of 2 min. The activated surfaces were graft polymerized in an aqueous solution of methacrylic acid at an initial monomer concentration in the range of [M]₀ = 5–20 vol% and temperature of 60–70 °C for a reaction period of ∼2 h for the SNS-PA-PEI–Si surfaces and 0.5 h for the SNS-PA-TFC membranes. Following the graft polymerization, the membranes were washed in DI water and stored in DI water until use.

It is important to note that, in the present method of graft polymerization, vinyl monomers are added to surface anchored polymer macro-radicals. Surface graft polymerization is initiated from surface active peroxide sites [27] that are activated by thermal initiation at a relatively low temperature to reduce homopolymer formation in solution [27]. For the above polymerization process, the rate of chain growth is dominated by the rate of monomer addition given by [20]

\[ R_{sp} = k_{sp}[SI]^{1/2}[M] \]  

where \( k_{sp} \) is a lumped propagation rate constant, [SI] is the concentration of activated surface which decompose thermally [20]. According to Eq. (1) the rate of grafted layer growth (due to monomer addition) is linear with monomer concentration which is expected to be the prevailing kinetics for low initial monomer concentrations. Although one would expect a low rate of thermal monomer initiation in solution, with increasing monomer concentration the rate of homopolymer chain growth can increase and thus contribute to the termination of surface chains with live homopolymer chains [20,27]. Above a critical initial monomer concentration, the increased rates of polymer grafting and surface-bound chain termination would reduce the number of surface anchored macro-radicals that can continue to grow by monomer propagation. As a consequence, chain growth would diminish, and the polydispersity of the surface grafted chains would increase. Therefore, one would expect an optimal initial monomer concentration at which the grafted polymer surface layer thickness and surface chain density would be adequate for screening the surface and also have sufficient Brownian motion capability to act as an effective antifouling layer.

### 2.4. Membrane surface characterization

The thickness of the grafted layer on the PA-PEI–Silicon wafers was determined by a Sopra GESS Spectroscopic Ellipsometer (SE) (Westford, MA). Water contact angles for the smooth PA-PEI–Si surrogate membrane surfaces were measured by the sessile-drop method (Kruess Model G–23 contact angle instrument) at 22 °C and 40–50% relative humidity. Water contact angles for the LFC1 and the SNS-PA-TFC membranes were measured by captive bubble method (Kruess Model DSA 100, Germany) at 22 °C. The membrane surfaces were characterized by Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy using a BioRad FTS-40 FTIR. Surface topography was evaluated by atomic force microscopy (AFM; Veeco Instruments, Santa Barbara) in tapping mode, in ambient air, using NSC15 silicon nitride probes with a force constant of ∼20–70 N/m, a nominal radius of curvature of 5–10 nm and a side angle of 20°. AFM scans of the 1 cm × 1 cm silicon substrates were taken at a scan rate of 0.5–1.0 Hz with at least five locations sampled for each substrate, with two scans taken for each location. Scan areas of 2 μm × 2 μm and 10 μm × 10 μm areas were taken for the relatively smooth SNS-PA-PEI–Si surfaces and the rougher SNS-PA-TFC membranes, respectively. Surfaces were imaged at 0° and 90° to verify that images were free of directional distortions.

The root-mean-square (RMS) surface roughness, \( R_{rms} \), was calculated from the height data and determined as

\[ R_{rms} = \sqrt{\frac{\sum (Z_i - Z_{avg})^2}{N}} \]  

where \( Z_i \) is the \( i \)th height sample out of \( N \) total samples and \( Z_{avg} \) is the average height. The skewness, \( S_{skew} \), which is a measure of the asymmetry of the height distribution data about the mean, was determined from

\[ S_{skew} = \frac{\sum (Z_i - Z_{avg})^3}{(N - 1) \cdot \sigma^3} \]  

where \( \sigma \) is the standard deviation. In order to provide a measure of the grafted polymer feature height distribution relative to the native substrate, the average Z-height of the native silicon surface (0.3–0.5 nm), determined from five locations for each surface, was subtracted from the surface feature height data for the polymer modified substrate. The adjusted Z-height data were then fitted to a Gaussian distribution to clarify the presence of tails (small or large features) in the distribution [20,21].

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**Fig. 1.** Thickness of graft polymerized poly(methacrylic acid) layer achieved by APPI-FRGP on PA-PEI–Si test surfaces at different initial MAA monomer concentrations and temperatures of 60 and 70 °C.
2.5. Membrane performance and gypsum scaling tests

Mineral salt scaling studies were conducted using a small plate- and-frame high pressure RO cell with an active membrane filtration surface area of 11.3 cm². All scaling tests were carried out at a feed cross-flow velocity of 0.19 cm/s delivered by a positive displacement pump from a feed reservoir kept at temperature of 25 °C using a refrigerated recirculator (Model 625, Fisher Scientific, Pittsburgh, PA). Transmembrane pressure was adjusted using a back-pressure regulator with a pressure dampener to reduce pressure fluctuations. Feed flow rate and pressure were measured using an electronic flow meter (Model K-32002-38, Cole-Parmer, Vernon Hills, IL) and a digital pressure gauge (Model D1005PS, Ashcroft, Milford, CT), respectively. Permeate flux was measured by collecting and measuring the filtrate weight with time using an electronic balance (Model ALC3100.2, Acculab, Arvada, CO) interfaced with a PC data acquisition system. The retentate was passed through a 0.2 μm microfilter as a precautionary measure to trap crystals that may have originated in the membrane channel and/or dislodged from the membrane surface, thereby focusing on gypsum scaling in the surface crystallization regime [1,2]. All membrane performance and gypsum scaling tests were conducted in a total recycle mode.

Prior to each membrane-scaling experiment, the test membrane was compacted in the RO cell by recirculating DI water through the system for 5 h at a feed cross-flow velocity of 0.19 cm/s and transmembrane pressure of 2070 kPa (300 psi). The membrane was then conditioned for a period of 2 h by circulating through the RO cell a feed solution of calcium chloride (5.23 g/l), with the permeate flux set at 2.95 × 10⁻⁴ cm/s. Subsequently, a predetermined volume of

Fig. 2. Column A: AFM images of PA-Si surfaces graft polymerized with poly(methacrylic acid) (at 60 °C and 2 h reaction time) for initial MAA monomer concentration of; (a) 5 vol%, (b) 10 vol%, and (c) 20 vol%. Column B: height distributions of the corresponding poly(methacrylic acid) grafted PA-PEI–Si surfaces also showing the Gaussian fit to the distribution based on the distribution portion to the left of the peak.
a Na₂SO₄ stock solution (5.05 g/l) was added to the feed reservoir to obtain a scaling solution that was super-saturated with respect to gypsum at Si₅ = 2. For the above feed solution, the induction time for bulk crystallization was above 20 h [28] which was significantly longer than the observed membrane-scaling times (<14 h) encountered in the present study. For all runs, the solution concentration over the entire membrane surface was at supersaturation (Sl₅ > 2). Therefore, mineral salt scaling under the above condition would continue until the entire membrane surface is scaled, with flux decline progressing until the permeate flux vanishes. Therefore, the time for the onset of mineral scaling was used in the present work to characterize the membrane-scaling propensity with scaling tests carried out for 11–14 h. Flux measurements continued until a measurable rate of permeate flux decline (15–35%) was observed to ensure that scaling has indeed occurred. For the above operating conditions, the present small RO cell functioned as a “differential RO Cell” with a negligible recovery such that the concentration at the membrane surface was essentially equal to that in the bulk. Membrane scaling was at the surface crystallization regime [2] at Sl₅ ≈ 2 which enabled the evaluation of flux decline due to mineral scaling over a reasonably short experimentation period [1]. All membrane-scaling studies were carried out, following established procedure [1], at the same initial permeate flux (2.95 × 10⁻⁴ cm/s) and cross-flow velocity (0.19 cm/s) such that the initial level of saturation at the membrane surface was identical for each scaling test. Finally, membrane hydraulic permeability and salt rejection for 1000 ppm NaCl and CaCl₂ salt solutions were measured, over a pressure range of 345–2070 kPa, before and post-gypsum membrane scaling (after the membrane has been cleaned by dissolving the gypsum crystals in DI water).

3. Results and discussion

3.1. Nano-structured poly(methacrylic acid) layer on polyamide

The effect of nano-structuring the active polyamide (PA) layer of thin-film composite (SNS-PA-TFC) membranes, with a layer of end-grafted poly(methacrylic acid) (PMMA) chains, on gypsum surface scaling propensity was evaluated in a series of membrane-scaling tests. The methacrylic acid graft polymerization reaction conditions, for the synthesis of the SNS-PA-TFC membranes, were first determined based on a series of graft polymerization tests with surrogate polyamide active layers interfacially polymerized onto smooth silicon wafer substrates with the aid of a PEI adhesion layer. This PA-PEI–Si surface was relatively smooth (Table 1) with a root-mean-square (RMS) surface roughness of 0.61 nm (relative to RMS = 0.21 nm for the silicon wafer), a mean feature height of about 1.5 nm and Sskew = 0.51 with a tail of feature heights in the range of 1–2 nm. The relatively smooth PA-PEI surface was adequate for characterizing the topography of the subsequent graft polymerized PMMA layer which was of thickness (5.2–7.1 nm) and RMS surface roughness of up to a factor of 3.8 greater than for the underlying PA-PEI surface (0.61 nm).

Graft polymerization of the PA-PEI–Si surface demonstrated that the surface polymer feature density and layer thickness for the end-grafted PMMA were highest, with the water contact angle being the lowest, at a short surface plasma exposure of about 10 s. MAA graft polymerization at 60 °C and initial monomer concentration of [Mₐ]₀ = 20 vol%. This result was consistent with earlier work [20] that demonstrated that the highest surface radical density with a hydrogen plasma was achieved at a relatively short exposure time of ~10 s. The end-grafted PMMA layer thickness reached a near plateau value in the range of 40–70 nm within a period of about 2 h (Fig. 1). The PMMA layer thickness increased with initial monomer concentration over the range of [Mₐ]₀ = 5–20 vol% (Fig. 1). As the reaction temperature increased from 60 to 70 °C, the polymer PMMA layer thickness was somewhat reduced. For example, a PMMA layer thickness reduction of 7.7% and 11.1% was observed for initial monomer concentration of 5 and 20 vol%, respectively, after the 2 h reaction period. It was previously suggested [20,21] that for free-radical graft polymerization, at higher reaction temperatures radical fragments, originating from the surface or via chain transfer (e.g., due to radicals in solution), may lead to the formation of polymer radicals in solution that may then bind to surface sites via polymer grafting and chain–chain combination reactions, thereby retarding polymer growth by chain propagation (i.e., sequential monomer addition). Accordingly, synthesis of the SNS-PA-TFC membranes is preferred at the lower temperature of 60 °C.

The distribution of polymer feature heights for the PMMA–PA-PEI–Si surface approached a Gaussian distribution with lower RMS surface roughness with increased initial monomer concentration (Fig. 2; Table 1). The PMMA layer feature peak density nearly doubled (average peak-to-peak separation distance decreased from 58 to 40 nm), the grafted layer thickness increased by ~36%, the RMS roughness and the skewness of the polymer feature height distribution both decreased by a nearly factor of 3, as the initial monomer

<table>
<thead>
<tr>
<th>Reaction conditions b</th>
<th>Rₑₑₑₑ (nm)</th>
<th>Sₑₑₑₑ (nm)</th>
<th>Polymer layer thickness (nm)</th>
<th>Contact angle (°)</th>
<th>All peak number density (feature/µm²)</th>
<th>Polymer feature diameter (nm)</th>
<th>Average peak-to-peak separation distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mₐ]₀ (vol%)</td>
<td>T (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>2.33</td>
<td>3.35</td>
<td>5.2</td>
<td>17</td>
<td>297</td>
<td>70–120</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
<td>1.50</td>
<td>2.05</td>
<td>6.3</td>
<td>13</td>
<td>463</td>
<td>50–80</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>0.88</td>
<td>1.10</td>
<td>7.1</td>
<td>10</td>
<td>650</td>
<td>10–30</td>
</tr>
</tbody>
</table>

a The PA-PEI–Si test surface had a peak number density of 619 (feature/µm²), polymer feature diameter in the range of 5–20 (nm) and RMS roughness of 0.61 nm, contact angle of 34°.

b 2 h reaction time.

Table 1

Poly(methacrylic acid) layer properties for the SNS-PA-PEI–Si surfaces.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Initial monomer concentration a ([Mₐ]₀ = vol%)</th>
<th>Rₑₑₑₑ (nm)</th>
<th>Contact angle (°)</th>
<th>Salt rejection b (%)</th>
<th>Lₑₑₑₑ (m/s Pa) × 10⁻¹⁰</th>
<th>tₑₑₑₑ (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFC1</td>
<td>−</td>
<td>73.4</td>
<td>48.5</td>
<td>94.4</td>
<td>1.5</td>
<td>4.5</td>
</tr>
<tr>
<td>SNS-PA-TFC (1)</td>
<td>5</td>
<td>58.5</td>
<td>49.5</td>
<td>94.5</td>
<td>3.4</td>
<td>5.8</td>
</tr>
<tr>
<td>SNS-PA-TFC (2)</td>
<td>10</td>
<td>70.2</td>
<td>43.2</td>
<td>95.4</td>
<td>3.1</td>
<td>10.2</td>
</tr>
<tr>
<td>SNS-PA-TFC (3)</td>
<td>20</td>
<td>80.7</td>
<td>48.4</td>
<td>95.8</td>
<td>2.0</td>
<td>6.9</td>
</tr>
</tbody>
</table>

All membranes exhibited salt rejection of ~95% as measured with CaCl₂. Note: SNS-PA-TFC membranes (1)–(3) were synthesized by APPIG-FRGP.

a Reaction period of 0.5 h at 60 °C.

b Salt rejection measured with [NaCl] = 1000 ppm.
Fig. 3. AFM membrane surface images along with the corresponding height distributions (showing Gaussian fit based on the left-and-side of the histogram). LFC-1 (a and e), SNS-PA-TFC membranes (Table 2): SNS-PA-TFC (1), b and f; SNS-PA-TFC (2), c and g; and SNS-PA-TFC (3), d and h.
concentration (for the graft polymerization reaction) increased from 5 to 20 vol% at 60 °C (Table 2). These results indicate that while the polymer feature density increased (and feature separation correspondingly decreased), with increasing initial monomer concentration, the polymer surface feature size (determined by AFM) decreased. The smaller feature diameter at higher initial monomer concentration is also consistent with the lower RMS surface roughness. It should be recognized that the size of the surface features, as determined by AFM imaging, is dictated, in part, by the collapsed “islands” of surface chains in air which is a poor solvent for the polymer [29]. A more uniform surface would therefore be consistent with the presence of less distinct and more uniform (and invariably of smaller diameter) surface polymer features. The above results demonstrated that the topography of the grafted PMAA layer (i.e., surface chain density and size) may be engineered by adjusting the initial monomer concentration, reaction temperature and reaction time.

3.2. Surface characterization and performance of SNS-PA-TFC membranes

Initial comparison of the scaling propensity of a number of selected commercial RO membranes (ESNA1-LF, ESPA1, TFC-ULP, LFC1; Section 2.3) revealed that the LFC1 membrane had the lowest scaling propensity among the selected commercial membranes (Fig. 4). The scaling induction time was 4.5 h for the LFC1 membrane compared to less than 1.75 h for the other commercial membranes. Therefore, the LFC1 membrane was selected as the baseline to evaluate the reduction in scaling propensity of the SNS-PA-TFC membranes that were synthesized in the present work.

The three SNS-PA-TFC membranes were synthesized at the same surface plasma exposure as for the surrogate SNS-PA-PEI-Si substrates, but a shorter reaction time of 0.5 h to keep the PA layer thickness below 4 nm (Fig. 1). The resulting membranes had surface roughness in the range of $R_{\text{rms}} = 58–81$ nm (Table 2), and surface feature height skewness reaching 0.78 (Fig. 3) for the range of initial monomer concentration of 5–20 vol%. The SNS-PA-TFC membranes prepared at initial monomer concentration of 5 and 20 vol% had about the same contact angle (49.5° and 48.4°) as for the commercial LFC1 membrane (48.5°). The slightly lower contact angle (43.2°) obtained for the SNS-PA-TFC membrane, prepared at 10 vol% initial monomer concentration, is within the uncertainty of the measurements (±5–10%), but could also point to some slight change in the surface chain density [30] that could not be ascertained via AFM surface imaging. The SNS-PA-TFC RO membranes had improved NaCl salt rejection (∼95%) compared to the pre-structured PA-TFC membranes which had a low salt rejection (∼30%) and therefore more appropriately classified as an NF membrane. The SNS-PA-TFC membrane permeability (Table 2) decreased from 3.4 to $2.0 \times 10^{-10}$ (m/s Pa) as the initial monomer concentration increased (5–20%, v/v) which in turn led to increased grafted layer thickness from 1.9 to 3.8 nm for the 0.5 h reaction time (Fig. 1). The two-step membrane surface structuring process was effective in raising the PA-TFC membrane performance to the level of a SNS-PA-TFC membrane of RO membrane characteristics (Table 2). The LFC1 membrane by comparison had RMS roughness of 73.4 nm and skewness of $S_{\text{skew}} = 0.72$. The presence of grafted PMAA was confirmed by FTIR spectra that revealed, for the SNS-PA-TFC membrane, the characteristic MAA peak at 1709 cm$^{-1}$, associated with the C=O group of the MAA carboxylic acids [13].

The salt rejection, based on NaCl, for the SNS-PA-TFC (94.5–95.8%) and the LFC1 (94.4%) membranes was similar as was the calcium rejection of ≥95% for the same membranes. However, the SNS-PA-TFC membranes demonstrated higher hydraulic permeability (2.0–3.4 × $10^{-10}$ m/s Pa) relative to the LFC1 RO membrane (1.5 × $10^{-10}$ m/s Pa) indicating that surface structuring with PMMA did not reduce the membrane water permeability, but in fact was beneficial in achieving a practical level of membrane permeability. The gypsum scaling propensity of the SNS-PA-TFC membranes was based on the observed time for the onset of mineral scaling as determined from the flux decline measurements described in Section 2.5 [32] (Fig. 5). The flux curves (Fig. 5) show that the “apparent induction time” for membrane scaling (i.e., the time at which flux decline commences) was $t_{\text{ind}} = 4.5$ h for the LFC1 RO membrane, while it was 5.8, 10.2 and 6.9 h, for the SNS-PA-TFC membranes prepared with $[\text{MAA}]_0 = 5, 10$ and 20 vol%, respectively. The above performance (scaling propensity reduction, salt rejection and permeability) was reproducible without observed performance loss over the several months of membrane testing.

One would expect the water permeability of the SNS-PA-TFC membranes to depend on the thickness of the grafted polymer layer and the associated surface chain density. Accordingly, it is reasonable to expect that increasing chain density and length would lower membrane permeability. As shown in Table 2, and supported by the result of Table 1, membrane permeability indeed decreased with increasing initial monomer concentration which in turn produced a thicker grafted layer. Based on the present set of SNS-PA-TFC membranes, the membrane synthesized at 10 vol% initial monomer concentration can be regarded as the best performing membrane. This selection was based on the fact that this membrane had a permeability that was only 9% lower than the highest permeability
SNS-PA-TFC membrane (Table 2), but with the lowest mineral scaling propensity (Table 2); the latter characteristics being of greater significance for applications of RO desalting for inland water of high mineral scaling potential.

Membrane-scaling propensity for the SNS-PA-TFC membrane was reduced (i.e., retardation of the onset of scaling) without having to achieve a significant reduction in surface roughness relative to a native PA-TFC membrane. It is hypothesized that the end-grafted PMAA chains, at the present level of surface coverage, provide sufficient surface screening of the polyamide surface, that in addition to the partial local mobility of the PMAA chains (in the aqueous solution), reduce the probability of nuclei and/or crystal lattice attachment to the end-grafted hydrophilic polymer layer surface; thus, the grafted chains are also likely to reduce bacterial adhesion. Verification of such a hypothesis, as a plausible mechanism for the observed retardation of the onset of surface scaling, would require direct observations of the membrane surface during the process of surface mineral salt crystallization. Such an endeavor is presently underway using a new approach of direct real-time membrane surface imaging [19,33].

It is important to recognize that mineral salt crystallization is unavoidable when the solution concentration at the membrane surface exceeds saturation, unless one utilizes antiscalants that retard the onset of nucleus and crystal growth [1,32]. In concert with the use of antiscalants, developing a membrane surface structure that can specifically retard the onset of mineral salt nucleation may enable one to operate membrane desalting operations at higher saturation levels, and thus at increased recovery as well as potentially reduced membrane cleaning frequency. Of course, the ultimate goal would be to simultaneously tune the membrane surface into reducing both mineral scaling propensity and organic and biofouling by optimizing the nano-structure of the membrane surface. Efforts in this direction are ongoing and will be reported in a future contribution.

4. Conclusions

An approach to surface nano-structuring of a reverse osmosis polyamide membrane was developed and demonstrated to enable reduction in membrane mineral scaling propensity, while retaining or even improving membrane water permeability relative to RO membrane performance at the same salt rejection level. The present approach is based on the activation of the base membrane polyamide active layer by exposure to an impinging source of the grafted chains are also likely to reduce bacterial adhesion. Verification of such a hypothesis, as a plausible mechanism for the observed retardation of the onset of surface scaling, would require direct observations of the membrane surface during the process of surface mineral salt crystallization. Such an endeavor is presently underway using a new approach of direct real-time membrane surface imaging [19,33].

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4. Conclusions

An approach to surface nano-structuring of a reverse osmosis polyamide membrane was developed and demonstrated to enable reduction in membrane mineral scaling propensity, while retaining or even improving membrane water permeability relative to RO membrane performance at the same salt rejection level. The present approach is based on the activation of the base membrane polyamide active layer by exposure to an impinging source of atmospheric pressure plasma, followed by free-radical graft polymerization of a hydrophilic water soluble monomer (methacrylic acid in the present work), under mild reaction conditions (60 °C) to form a layer of end-grafted poly(methacrylic acid) (PMAA) surface layer. The PMAA layer thickness, as determined from studies with smooth PA test surfaces, was in the range of 5.2–7.1 nm, with skewness of the surface feature height histogram for the SNS-PA-TFC membranes of Skew up to 0.78. The SNS-PA-TFC membranes were of permeability that was significantly higher (by up to a factor of ~2) relative to the low fouling commercial membrane of about the same level of salt rejection. However, the time for the onset of gypsum scaling of the SNS-PA-TFC increased significantly by a factor of 2~5 relative to the commercial TFC membranes. The present approach to PA-TFC membrane surface nano-structuring is simple to apply, given the operation under atmospheric conditions, impinging plasma source, and low temperature graft polymerization reaction, and thus has the potential for adaptability to commercial scale membrane production [34,35]. Current work is ongoing to further optimize the surface structure to increasing scaling and biofouling resistance, reduce the graft polymerization reaction time, and also clarify the mechanism involved the reduction of membrane-scaling propensity.

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References