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Dendrimeric Thin-Film Composite Membranes: Free Volume, Roughness, and Fouling Resistance

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KEYWORDS

polyamide, interfacial polymerization, dendrimer, polyamidoamine, fouling resistance

ABSTRACT

Copolyamide films with a thickness from 50 to 780 nm were fabricated by interfacial polymerization between mixtures of m-phenylene diamine and primary amine-terminated polyamidoamine dendrimers (PAMAM) in the aqueous phase and trimesoyl chloride (TMC) in the organic phase. Different PAMAM generations (G0, $d = 15 \text{ \AA}$, $Z = 4$; G3, $d = 36 \text{ \AA}$, $Z = 32$; and G5, $d = 54$, $Z = 128$, where d is the measured diameter and Z is the number of terminal groups) and concentrations were used to obtain copolyamide films with different crosslinked structures. The influences of the concentration and degree of branching (PAMAM generation) on free volume were analysed via positron annihilation spectroscopy (PAS) and correlated with the separation properties of copolyamide films. Besides, surface and intrinsic properties of copolyamide films prepared under different conditions were compared. The high hydrophilicity of PAMAM in the copolyamide network leads to the formation of a hydration layer on the copolyamide surface, which minimizes fouling. The separation performance of copolyamide membranes with various PAMAM networks was investigated in forward osmosis (FO) experiments. Understanding the correlation between the PAMAM structure/concentration, free volume, thickness, and surface intrinsic properties leads to the design of suitable fouling resistant thin-film composite membranes in a single interfacial polymerization process.

1. INTRODUCTION

Thin film composite (TFC) membranes have been widely used for wastewater treatment and desalination in nanofiltration (NF),¹ reverse osmosis (RO),² and forward osmosis (FO)³⁻⁸ processes, because of their (i) high water permeance and good selectivity, compared to integrally skinned asymmetric membranes, (ii) simple and fast fabrication process, and (iii) high flexibility in membrane design with independent optimization of selective layers and porous supports. However, polyamide TFC membranes are prone to fouling, which is caused by the undesirable adsorption and deposition of various types of contaminants in the feed, including inorganic and organic compounds, particles, and microorganisms.⁹ Membrane fouling leads to an increase of the mass transfer resistance, significantly decreasing the membrane performance, reducing its life, and increasing pre-treatment and cleaning costs. Therefore, prevention of undesired foulants adhesion on the polyamide surfaces remains a big challenge for the use of TFC polyamide membranes in contaminated water separation processes. Changing the polyamide surface to make it more hydrophilic and/or smoother is crucial to mitigate the foulant – membrane surface adhesion.

A polyamide layer is commonly formed on a porous substrate by immersing it in an aqueous solution, containing diamines, followed by immersion in a non-polar solvent solution containing an acid chloride. At the interface between the aqueous and organic solutions, interfacial polymerization between diamine and acid chloride monomers takes place, forming a thin polyamide layer. The separation performance and the fouling resistance of polyamide membranes are strongly influenced by their surface intrinsic properties (i.e., hydrophilicity, roughness, charge, pore size) and by the layer free volume and thickness. The polyamide film properties are controlled by varying the interfacial polymerization conditions such as reaction

time, monomer concentration,¹⁰ monomer structure,^{2, 11} additive,¹² and post-treatment conditions.³ Membranes with enhanced fouling resistance have been recently developed by incorporation of tris (2-aminoethyl)amine (TAEA) hydrophilic amine monomer,¹³ anti-microbial photo-responsive amine terminated monomer,¹⁴ and hydrophilic nanoparticles such as UiO-66¹⁵ and graphene oxide quantum dot.¹⁶ Various techniques have been investigated for polyamide surface modification including surface grafting of graphene oxide,¹⁷⁻¹⁸ polyethyleneimine (PEI),¹⁹ zwitterionic polymer,²⁰ coating with polydopamine,²¹ followed by UV irradiation treatment,²² and Al₂O₃ atomic layer deposition.²³ Another strategy to increase fouling resistance of polyamide layers is to use plasma treatment. Examples are plasma polymerization²⁴ and low pressure argon plasma surface activation.²⁵

Dendrimers are highly branched spherical macromolecules containing plenty of reactive functional groups. Like conventional polymers, dendrimers have repeating units, but in three-dimensional and regularly branched structures. A dendrimer contains three distinct regions, including a core, a layer of repeating units, and an outer layer with end functional groups.²⁶ Among various investigated classes of dendrimers, primary amine-terminated polyamidoamine dendrimers (PAMAM) dendrimers are the most extensively researched dendrimers, after the pioneer work of Tomalia²⁷ in 1985. PAMAM dendrimers of up to 10 generations can be produced with narrow molecular weight distribution and a variety of functional terminal groups, which are convenient for further surface modifications or for synthesis of more complex structures. Because of their unique properties, PAMAM dendrimers have been used for numerous applications, such as drug and gene delivery,²⁸⁻²⁹ biological imaging,³⁰ catalysis,³¹ sensors,³²⁻³³ gas separation,³⁴⁻³⁵ and wastewater treatment.³⁶⁻³⁹ Grafting PAMAM dendrimers on the surface of a pre-formed thin-film composite membrane has been reported to increase

hydrophilicity and reduce roughness. As the PAMAM dendrimer generation increases, the hydrophilicity of PAMAM grafted polyamide layer increases and this may potentially enhance the membrane fouling resistance.⁴⁰

Our aim is to prepare highly fouling resistant and permeable TFC membranes, using a one-step simple interfacial polymerization process without the need of further modification. Mixtures of m-phenylene diamine (MPD) and primary amine terminated PAMAM dendrimers (Figure 1) were used as amine monomers to react with acid chloride to form highly hydrophilic and permeable copolyamide films on the top of a porous PES support. The copolyamide TFC membrane performance and fouling behaviour in FO experiments were investigated.

2. EXPERIMENTAL SECTION

Materials

Polyethersulfone (PES, BASF), N-methyl-2-pyrrolidone (NMP, Alfa Aesar), polyethylene glycol (PEG₄₀₀, M_w 400, Sigma-Aldrich) were used as received for PES support fabrication. Trimesoyl chloride (TMC), m-phenylene diamine (MPD), ethyl acetate, and n-hexane were obtained from Sigma-Aldrich and used for the synthesis of the polyamide layer by interfacial polymerization. Sodium chloride (NaCl) was obtained from Merck (Germany). Primary amine-terminated polyamidoamine (PAMAM) dendrimers with various generations (0, 3, and 5) were purchased from Dendritech. Polyester woven fabric with a nominal hole size of 50 µm and a thickness of 60 µm (WS0050) was supplied by Industrial Netting. Fluorescein isocyanate conjugated bovine serum albumin (BSA-FITC), soybean oil, and tween 80 were supplied by Sigma-Aldrich.

Figure 1. Molecular structures of primary amine-terminated polyamidoamine (PAMAM) dendrimers (a) generation 0 and (b) generation 3.

Table 1. Properties of primary amine PAMAM dendrimers

Dendrimer	Generation	Molecular weight (g/mol)	Measured diameter (Å)	Surface groups, Z
PAMAM G0	0	517	15	4
PAMAM G3	3	6,909	36	32
PAMAM G5	5	28,826	54	128

Preparation of PES membrane supports

Woven-embedded PES membrane supports were fabricated via non-solvent induced phase separation using the co-casting technique (Figure 2a).

Figure 2. (a) Schematic illustration of co-casting woven-embedded PES membrane support and (b) its FESEM micrographs: cross-section (C), surface (S, top and bottom).

A woven fabric with a thickness of $60 \mu\text{m}$ was firstly adhered to a glass plate. Two polymer solutions, PES/PEG400/NMP/water ($7.0/44.6/47/1.4$, wt%) and PES/PEG400/NMP/water ($14.9/38.5/43.6/3.1$, wt%) were co-spread onto the woven fabric at the same time, using two casting knives. The low concentration polymer solution was placed in front and spread with a 60 or $100 \mu\text{m}$ gap casting knife. The high concentration polymer solution was placed right behind and spread on the as-spread low concentration film with a 150 or $200 \mu\text{m}$ gap casting knife. The

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2
3 multilayer system was immersed in a water coagulant bath overnight for complete precipitation,
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5 as well as additive and solvent removal.
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8 9 **Thin-film composite membrane preparation**

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12 The membranes were prepared by deposition of pristine or PAMAM-modified polyamide films
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14 on woven-embedded PES membrane supports via interfacial polymerization. Different PAMAM
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16 generations and concentrations were blended with MPD to produce amine-containing aqueous
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18 solutions, having a total amine concentration of 2 wt% in water. TMC was dissolved in 3 wt%
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20 ethyl acetate in hexane solution at a concentration of 0.15 wt% TMC, and was used as the
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22 organic solution for interfacial polymerization. PES supports were immersed in the aqueous
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24 solutions for 5 min and followed by the removal of excess solution on the support surfaces.
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26 Subsequently, the organic solution was poured on top of the amine-containing PES supports for
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28 1 min to induce the formation of polyamide layers. The membranes were dried in open air for 1.5
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30 min to complete the interfacial polymerization process and washed with DI water to remove
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32 unreacted amines.
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39 **Free-standing polyamide thin-film composite fabrication**

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42 Free-standing polyamide films were prepared by bringing the organic solution into contact with
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44 the aqueous solutions for 6 h. The organic solution contained 0.15 wt% TMC and 3 wt% ethyl
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46 acetate in hexane. The aqueous solutions contained MPD and/or dendrimers with the total
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48 concentrations of 2 wt% in DI water. The interfacial polymerization took place at the interface
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50 between the two solutions, forming the polyamide films. The polyamide films were rinsed with
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52 DI water and stored at 4 °C.
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Characterization of membranes and free-standing films

The surface and cross-section of polyamide membranes and free-standing films were imaged by field-emission scanning electron microscopy (FESEM) on Quanta 600 FEG and Nova™ NanoSEM 630 (FEI, USA) microscopes. For cross-section imaging, samples were fractured in liquid nitrogen. All samples were freeze-dried and coated with iridium before imaging.

The surface roughness was determined by atomic force microscopy (AFM) on an Agilent 5400 SPM, Agilent Technologies) equipment. Freeze-dried membranes were analyzed under the tapping mode with a silicon probe. Pico Image software was used to calculate the mean roughness (Ra) and the root mean squared roughness (Rq) of membrane surfaces.

The membrane surface hydrophilicity was estimated by measuring the water contact angle of the freeze-dried membranes using a Krüss Easydrop (Krüss GmbH).

The differences in membrane surface chemistry of the pristine and PAMAM modified polyamide membranes were determined by attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR, Nicolet™ iS™10 FT-IR spectrometer, Thermo Scientific, USA).

Slow beam positron annihilation spectroscopy (PAS) was used to compare the free volume of different polyamide layers, formed on the TFC membranes. Doppler broadening energy spectroscopy (DBES) PAS was used to detect the changes in free volume and its variation as a function of depth profile. The DBES spectra as a function of positron incident energy ranging from 0 to 30 keV were obtained using an HP Ge detector. From the DBES spectra data, the R and S parameters, which are defined as the ratio of the total counts from an energy width between 364.2 and 496.2 keV (due to ortho-positronium (o-Ps) 3γ annihilation), and the

integrated counts at the central part between 510.3 keV and 511.7 keV of the annihilation gamma photo line, respectively to the total counts from the 511 keV peak region (due to 2γ annihilation), was used to evaluate the porosity and free volume.⁴¹

Fouling

Static fouling experiments were conducted at room temperature (23 ± 1 °C), using BSA-FITC as a model organic foulant. The adsorption of BSA on the pristine and PAMAM G0 polyamide membrane surfaces was evaluated by the fluorescence signal of the membrane surfaces, after 1 h exposition to a 200 ppm BSA-FITC solution. The BSA-FITC adsorbed membranes were imaged using a Leica SP5 laser scanning confocal microscope (Leica Microsystems) with the excitation and emission wavelengths of 495 and 519 nm, respectively. The amount of adsorbed BSA-FITC on membrane surfaces was evaluated using ImageJ software. In addition, the fluorescence intensity of the adsorbed BSA-FITC on membrane surfaces was measured by a Varian Cary Eclipse fluorescence spectrophotometer (Agilent, USA) with the excitation and emission wavelengths of 490 and 515 nm, respectively.

Dynamic fouling experiments were performed using a lab-scale FO set-up at a cross-flow velocity of 10 cm/s. An oily feed solution was used as a feed model containing high concentration of foulant. The oily feed solution was prepared by emulsifying soybean oil and tween 80 in 1000 ppm NaCl solution to form a 2000 ppm oil in water (OiW) emulsion, as previously described.⁹ Baseline experiments using DI water as the feed solution were conducted at the same testing conditions as the fouling tests. The extent of flux decline associated with the oil particle adsorption was evaluated by normalizing the fouling data to the baseline data.

Membrane performance

The membrane performance in FO processes was investigated at room temperature on a lab-scale cross-flow FO set-up, using 1M NaCl as the draw solution and DI water as the feed. Feed and draw solutions flowed counter-currently on each side of the membrane. Water flux (J_v , $\text{Lm}^{-2}\text{h}^{-1}$, abbreviated as LMH) and reverse salt flux (J_s , $\text{gm}^{-2}\text{h}^{-1}$, abbreviated as gMH) were measured using the following equations:

$$J_v = \frac{\Delta V}{A_{\text{eff}} \Delta t} \quad (1)$$

and

$$J_s = \frac{\Delta(C_t V_t)}{A_{\text{eff}} \Delta t} \quad (2)$$

where ΔV (L) is the water volume that has permeated across the membrane in a predetermined time Δt (h), during the tests. A_{eff} is the effective membrane surface area (m^2). C_t and V_t are the salt concentration (g/L) and the feed volume (L) at the end of the tests, respectively. The feed conductivity was measured by a ProfiLine Cond 3310 conductometer (WTW, Germany).

3. RESULTS AND DISCUSSION

TFC membranes for RO desalination, NF water purification or FO processes typically have an asymmetric structure with a selective dense skin and a porous bottom, which here are the polyamide layer and PES support, respectively. The performance of the membrane is controlled by intrinsic properties of the selective layer and the support. In this work we propose strategies to tailor both the support and the selective layer, aiming at a perfectly optimized TFC membrane for osmotically-driven processes.

Table 2. Performance of FO membranes prepared from various supports, using 1 M NaCl as draw solution and DI water as feed. Polyamide layers were prepared from MPD/TMC.

Co-cast PES layers: Solution layer thicknesses: High/low conc.	PRO mode	
	Water flux (LMH)	Reverse salt flux (gMH)
200 μ m /60 μ m	29 $\pm$ 3	13 $\pm$ 1
200 μ m /100 μ m	50 $\pm$ 1	14 $\pm$ 2
150 μ m /100 μ m	Defects	
150 μ m /0 μ m	23 $\pm$ 1	9 $\pm$ 2

As far as the support is concerned a more open-structural would produce low transport resistant and minimal internal concentration polarization and lead to high water permeance. Using low PES concentration during the support casting results in a highly porous support with a large surface pore size. Too large pores on the support surface may cause defects on the subsequent polyamide film formation via interfacial polymerization. In addition, a low polymer concentration in the casting solution can compromise the support mechanical properties. In order to circumvent the drawback associated with the low concentration casting solution and reach high permeation characteristics and a defect-free selective layer, a co-casting technique (Figure 2a) was chosen in this work, performed on a thin and open woven fabric with strong mechanical strength. A 7 wt% PES solution was used as a sacrificial layer, co-cast beneath a PES solution with higher concentration (14.9 wt%). The thickness of the co-cast layers needs to be optimized to obtain a defect-free support with high performance. As shown in Table 2, when solutions with 14.9 and 7.0 wt% PES were co-cast using doctor blades with respectively 200 and 60 μ m gaps, the resulting membranes, after interfacial polymerization, had lower FO performance than those

cast with 200/100 μm gaps. Further reducing the casting gap of the 14.9 wt% top layer to 150 μm led to defect formation, while casting of a single layer with the same gap and concentration resulted in a defect-free membrane. The best results were obtained with 200/100 μm gaps, which led to defect-free membranes and good FO performance. These membranes were chosen as support for subsequent studies.

The morphology of the PES support, co-cast with 200/100 μm gaps (woven-embedded PES) is shown in Figure 2b. The cross-section image indicates that the obtained PES support has a thickness of approximate 80 μm and an asymmetric structure with finger-like macrovoids. The surface SEM images show uniform 10 – 20 nm pores on the top and a bottom with open structure, indicating suitable characteristics for the consequent polyamide formation. Open support porosity would be convenient to reduce the membrane propensity to concentration polarization in FO operation, facilitating the removal of accumulated foulants from the bottom.

Table 3. Performance of FO membranes using 1 M NaCl as draw solution and DI water as feed

Membrane	PRO mode		FO mode	
	Water flux (LMH)	Reverse salt flux (gMH)	Water flux (LMH)	Reverse salt flux (gMH)
Pristine	50 $\pm$ 1	14 $\pm$ 2	22 $\pm$ 2	8 $\pm$ 1
PAMAM G0	52 $\pm$ 2	16 $\pm$ 2	23 $\pm$ 2	10.0 $\pm$ 0.7
PAMAM G3	42 $\pm$ 3	23 $\pm$ 2	19 $\pm$ 3	16 $\pm$ 3
PAMAM G5	40 $\pm$ 3	26 $\pm$ 6	18 $\pm$ 1	17 $\pm$ 6

Figure 3. FESEM surface (S) and cross-section (C) images of (a) pristine; (b-d) PAMAM G0, G3 and G5 membranes.

Once the support was optimized, thin polyamide layers were formed by interfacial polymerization using different ratios of PAMAM with various molecular weights, and number of branches and functional groups (generations), as shown in Table 1 and Figure 1. We demonstrate how these factors affect the final selective layer properties. Pristine, PAMAM G0, PAMAM G3, and PAMAM G5 polyamide membranes are compared in Table 3, as well as in Figures 3 and 4. For the interfacial polymerization 1 wt% amine solutions containing only MPD (pristine membrane) or 10 wt% PAMAM (90 wt% MPD) of generations G0, G3, or G5 were used. The morphology and thickness of the polyamide films are shown in Figure 4. Continuous and defect-free selective layers with crumpled nodular structures are seen for pristine and all PAMAM-modified membranes. Compared to the pristine membrane, PAMAM G0 membrane has a similar polyamide thickness and morphology. By increasing the generations of PAMAM, the polyamide

thickness reduces in the order of PAMAM G0 > PAMAM G3 > PAMAM G5 while its surface nodular features become larger and smoother, following the same trend.

Figure 4. AFM topographical images of (a) Pristine, (b) PAMAM G0, (c) PAMAM G3, and (d) PAMAM G5 membranes; (e) their surface mean roughness and (f) water contact angle.

The topographic images of the polyamide surfaces, obtained by AFM, give us a more quantitative information on their mean roughness values (Figure 4a – e) and how they depend on the PAMAM generation. PAMAM G5 polyamide layers are almost two-fold thinner and smoother compared to the pristine one. When the generation increases, PAMAM becomes bulkier with a higher density of amine groups. The higher density of amine groups may result in a dense polyamide film formed at the initial stage of interfacial polymerization, reducing the further diffusion rate of amine molecules into the organic phase. In addition, PAMAM of higher generation are bulkier, what also contributes to a slow transferring rate to the organic phase. The

slow transport rate of amine-terminated molecules leads to less local convection, favouring a smoother and thinner film. PAMAM dendrimers are highly hydrophilic. PAMAM dendrimers are known to have a large number of bound water molecules on external sites and or more in the interior (approximately 114 to 148 hydrogen bonds between water molecules and unprotonated or a protonated PAMAM G3 molecule, respectively).⁴² For the interfacial polymerization the primary amines are partially consumed, but at least the secondary amino groups still remain available for a strong interaction with water. The high binding density of water molecules leads to the formation of a denser hydration layer on the copolyamide surface. Therefore, the water contact angle of polyamide films reduces from approximate 75 ° for the pristine membrane to approximate 62 ° for PAMAM G0 – G5 modified membranes, as shown in Figure 3f.

We investigated how the membrane performance in osmotically-driven processes is affected by the dendrimer generation. This was demonstrated for FO experiments, in which feed and draw solutions flow on the two opposite sides of the membranes. FO and PRO (pressure retarded osmosis) modes correspond to different orientations of the polyamide layer facing the draw solution or the feed. The results are shown in Table 3 for the pristine and PAMAM G0 – G5 membranes. The difference in the performance of the four membranes in Table 3 is ascribed to whole set of polyamide properties, including hydrophilicity, surface roughness, layer thickness, which has been discussed above. The FO performance results in Table 3 and Figures 3 and 4 show that the incorporation of PAMAM G0 in the polyamide network increases the membrane hydrophilicity and slightly reduces the surface roughness without compromising the performance. Compared to PAMAM G0, the high-generation PAMAM dendrimers are more difficult and expensive to produce. Therefore, we opted to optimize the PAMAM G0 membrane as a good choice for water flux improvement and fouling resistance modification. PAMAM G0

membranes with dendrimer ratios to MPD ranging from 0 to 100% were investigated. The chemistry changes of PAMAM G0 membranes at different dendrimer concentrations were investigated using ATR-FTIR to confirm the increase in the amount of incorporated dendrimer in the polyamide film using a high dendrimer concentration during the interfacial polymerization. The results are shown in Figure 5. Increasing dendrimer concentration causes the reduced aromatic breathing peaks (1490 cm^{-1} and 1610 cm^{-1}), the shifting of amide I peak from 1660 cm^{-1} (characteristic peak of the pristine polyamide) to 1640 cm^{-1} (characteristic peak of 100% PAMAM G0 polyamide), and the broaden of amide II peak (1530 cm^{-1}) due to the abundant of NH group in PAMAM chains. The ATR-FTIR results confirm the increase of PAMAM concentration in the polyamide network when using higher PAMAM ratios.

Figure 5. FTIR spectra of different PAMAM G0-modified PA layers.

Smoother and thinner polyamide films were formed with higher PAMAM G0 ratios as shown by FESEM (Figure 6) and AFM (Figure 7). The thickness of the polyamide significantly reduces from 780 nm for 0% PAMAM G0 membrane to $<50\text{ nm}$ for 100% PAMAM G0 membrane,

leading to low transport resistance and high flux in FO experiments. With a typical ridge-valley crumpled structure, 0% PAMAM G0 membrane surfaces have an average roughness of 123 nm, which is reasonable for a polyamide film prepared from MPD and TMC. The polyamide film roughness reduces as the PAMAM G0 ratio increases. The smoothest polyamide film with an average roughness of 7 nm was obtained with 100% PAMAM G0. Higher PAMAM G0 concentration increases the hydrophilicity of the TFC membrane surface.

Figure 6. FESEM images of the surface (S) and cross-section (C) of PAMAM G0 modified membranes, using various ratios of PAMAM dendrimer G0 (relative to MPD wt %).

Figure 8 shows the water contact angle data for 0 – 100% PAMAM G0 membranes. The water contact angle values reduce from 75 ° (0% PAMAM G0 membrane) to 34 ° (50% PAMAM G0

membrane), which is consistent with the increased hydrophilicity of PAMAM G0 membrane at high dendrimer concentration. The 100% PAMAM G0 membrane has slightly higher water contact angle value (approximate 40 °) than the 50% PAMAM G0 membrane. We need to take into consideration that the water contact angle is influenced not only by the presence of hydrophilic groups, but also by the surface roughness. According to Wenzel model, surface roughness would contribute to the membrane wetting property. The hydrophilic membrane having a contact angle of $< 90^\circ$ would have even lower contact angle, when increasing the surface roughness. When membranes have similar and low contact angles, the one with smoother surface, as in the case of the 100% PAMAM G0, would have higher contact angle.

Figure 7. AFM topographical images and surface mean roughness of PAMAM G0 membranes, using various PAMAM G0 ratios (relative to MPD wt%).

Figure 8. Contact angles of various PAMAM G0-modified PA surfaces.

In addition, free volume might be an essential factor. The determination of the free volume of polymer layers as thin as those prepared in this work has been always a challenge. Very few methods can be used to quantify it. Indirect measurement of free volume has been reported using fluorescence probes.⁴³ PAS is currently the most effective experimental method for free volume quantification. However until recently PAS was mainly a bulk characterization method, requiring samples with high thickness, being unsuitable for asymmetric TFC membranes. Kim et al. stacked TFC membranes using a maximum entropy lifetime analysis method, being the first to be able to provide free volume by PAS for this kind of membranes. In a pioneer work Chen et al.⁴⁴ combined DBES and PAS to measure free volume of TFC membranes as a function of depth. The method has been explored by only a few groups⁴⁵⁻⁵⁰ and has been chosen as the most convenient in this work.

Figure 9. (a) R and (b) S parameters of PAMAM G0-modified PA membranes prepared with different PAMAM G0 ratios (relative to MPD).

The porosity of 0 – 100% PAMAM G0 membranes was compared in Figure 9, based on PAS data. The R values give information on the porosity (cavities in the nm and μm range) profile of the membrane. Near the membrane surfaces, the R values for all curves sharply decrease with the increase of positron incident energy. The R values reach minimum values at around 2.5 keV, keeping a relatively low value until 5 keV. This range of positron incident energy, according to previous PAS reports,⁵¹ leads to a sampling depth around 240-480 nm, which is the region occupied by the dense polyamide layer. Subsequently, the R values increase to a plateau and attain maximum values at around 8 keV, corresponding to a transition layer between the dense polyamide thin film and the porous PES support. Finally, the R parameter values slowly decrease, indicating that the density of large cavities or pores decreases as the depth of the PES membrane increases, approaching the bottom. The lower minimum R parameter value can be

seen in the PAS curve of membrane with the highest PAMAM G0 ratios. The highest R value in the intermediate layer was observed for the pristine membranes, indicating a more open or more porous structure. The lowest R value in the depth corresponding to the thin polyamide layer was observed for the membranes with 100 wt% PAMAM G0, followed by those with 50 wt% PAMAM G0. In order to better quantify the free volume of the dense polyamide layers the S parameters were plotted as a function of energy (Figure 9b). The S values, and hence the free volumes, decrease in the following order: 0 wt% > 20 wt% > 50 wt% > 100 wt% PAMAM G0.

Table 4 shows the FO performance of PAMAM G0 membranes with varying dendrimer ratios. TFC membranes with different PAMAM G0 ratios up to 20% exhibit very similar water fluxes both in the FO and PRO modes. The increased hydrophilicity and reduced polyamide thickness are dominant factors contributing to the final FO performance. Contradictorily, further increasing of the PAMAM G0 ratio significantly reduced the water flux. The membrane reverse salt flux is affected by PAMAM G0 ratio as well, with a slight increase when changing the dendrimer ratio from 0 to 50%. Specially, very high reverse salt flux is observed for the 100% PAMAM G0 membrane. By preparing free-standing films by interfacial polymerization with the same compositions and imaging the bottom surface, we observe that all polyamide layers with PAMAM G0 ratios between 0 and 50% have relatively dense and smooth bottom surfaces (Figure 10a – e), while the 100% PAMAM G0 polyamide film contains big pores or pin holes (Figure 10f). This could explain the poor rejection of 100% PAMAM G0 membranes.

Table 4. Performance of FO membranes using 1 M NaCl as draw solution and DI water as feed

PAMAM G0 content (%)	PRO mode		FO mode	
	Water flux (LMH)	Reverse salt flux (gMH)	Water flux (LMH)	Reverse salt flux (gMH)
0	50 ± 1	14 ± 2	22 ± 2	8 ± 1
5	50 ± 1	16 ± 1	22 ± 2	10 ± 2
10	52 ± 2	17 ± 2	23 ± 2	10.0 ± 0.7
20	51 ± 2	18 ± 4	23 ± 1	12 ± 2
50	41.5 ± 0.8	30 ± 6	20 ± 3	20 ± 1
100	23 ± 3	260 ± 43	17 ± 3	160 ± 16

Figure 10. FESEM surface images of the bottom of free-standing G0 modified polyamide films, using various ratios of PAMAM G0 (relative to MPD).

The fouling behavior of the pristine (0% PAMAM G0) and PAMAM G0 modified membranes were compared using BSA protein and emulsified oil particle as model foulants. The attachment of foulants onto the selective membrane surfaces was conducted in static and dynamic modes, in

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3 which the fouling propensity is mainly controlled by the polyamide hydrophilicity and the
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5 combinative effects of the polyamide hydrophilicity and surface roughness, respectively. The
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7 static BSA adsorption at neutral pH 7.4 onto the pristine and PAMAM G0 modified surfaces was
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9 compared by analyzing the FITC fluorescence signal from BSA-FITC molecules bonded to the
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11 membrane surfaces. Figure 11a shows the confocal images of membranes exposed to BSA-FITC,
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13 with the green signal representing higher fluorescence signal. The relative BSA adsorption was
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15 analyzed from the confocal images, using ImageJ to give more comparative information on the
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17 controlled fouling of PAMAM G0 membranes (Figure 11b). The fluorescence intensity was also
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19 quantified by using fluorescence spectroscopy and the data are presented in Figure 11c. Using
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21 different methods to characterize the fouling behavior of the membranes towards BSA, the same
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23 fouling trend is observed. When the PAMAM G0 ratio in the polyamide network is higher,
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25 weaker fluorescence intensity is observed. At neutral pH, the membrane zeta potential becomes
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27 less negative as the PAMAM content in the polyamide layer increases, as shown in Table 5. This
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29 is due to the presence of tertiary amines and non-reacted protonated primary amines in the
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31 PAMAM building blocks. The hydrophilicity of PAMAM dendrimers promotes the binding of
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33 more water molecules to the surface, creating a hydration boundary that partially hinders the
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35 attachment of more hydrophobic/negatively charged protein molecules on the less negatively
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37 charged PAMAM polyamide surface.
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Figure 11. (a) Confocal images, (b) relative protein adsorption quantified from confocal images, and (c) relative protein adsorption quantified from fluorescence spectroscopy of the pristine and various PAMAM G0-modified PA surfaces after 1 h exposure to BSA-FITC solutions.

The effect of PAMAM in the polyamide layer on controlling the foulant deposition during the dynamic separation condition at flow rate of 100 mL/min, was investigated using a feed solution containing 2000 ppm oil in water emulsion with the initial water flux of approximate 20 LMH. The baseline tests were carried using DI water as the feed. The effects of the decreased osmotic driving force and the diluted draw solution, during fouling tests, were eliminated from the fouling data by subtracting the baseline data.

Table 5. Zeta potential of PAMAM G0 modified membranes at neutral pH (pH 7)

PAMAM G0 content (%)	Zeta potential (mV)
0	-29.7
20	-20.0
50	-12.5
100	-3.3

Figure 12. Flux decline curves in fouling experiments, using synthetic oil in water emulsion as feed, containing 2000 ppm oil and 1000 ppm NaCl. The water fluxes were normalized by the base line, to account for the draw solution dilution and the osmotic driving force decrease during the tests.

Figure 12 shows the flux decline curves for membranes prepared from 0 and 20% PAMAM G0, during the fouling tests, after the baseline subtraction. Compared to the pristine membrane (0%

PAMAM G0), the 20% PAMAM G0 membrane has slower flux decline, indicating its higher fouling resistance. The high surface roughness of the pristine membrane leads to high propensity to entrap foulants and prevent their removal by hydrodynamic force. Moreover, the pristine membrane has lower hydrophilicity and may attach more oil due to hydrophobic interaction, leading to higher fouling.

Table 6 summarizes the performance of the 20% PAMAM G0 modified membrane (PAMAM TFC), commercial TFC membrane, and recently published membranes with modifications on the polyamide layers or support layer. Compared to the commercial TFC membrane, the PAMAM TFC membrane surpasses the water flux in both PRO and FO modes while having comparable rejection. Among polyamide modified TFC membranes (PAMAM TFC, TAEA TFC, Halloysite nanotubes TFC), the membrane reported in this work shows higher performance with additional mechanical stability benefited from the embedded woven fabric.

Table 6. Comparisons of FO performance of various flat-sheet TFC membranes

Membrane	Fabric support	Water flux PRO/FO (LMH)	Reverse salt flux PRO/FO (gMH)	Feed/Draw solutions	References
PAMAM TFC	Woven	51/23	18 /12	DI water/1 M NaCl	This work
TAEA TFC	No	51.7/26.9	15.5/9.3	DI water/2 M NaCl	52
HTI TFC	Non-woven	33/15	17.5/7.5	DI water/1 M NaCl	53
sPPSU TFC	Woven	47.7/30.5	-/-	DI water/1 M NaCl	54
Block copolymer TFC	No	74.4/40.5	11.8/9.3	DI water/2 M NaCl	55
Halloysite nanotubes TFC	No	43.2/27.7	27.5/14.6	10 mM NaCl/2 M NaCl	56

4. CONCLUSIONS

The effect of the PAMAM dendrimer generation and ratio on the performance and fouling resistance of TFC membranes has been demonstrated in this work. The thickness, hydrophobicity, and surface roughness of the polyamide layer could be reduced by incorporating dendrimers of increasing generation. Analogous trend was observed by keeping the generation constant (G0) and increasing the dendrimer concentration. For G0 membranes the free volume decreased as the dendrimer ratio increased, as confirmed by PAS/DBES. The increase of the fouling resistance with the increase of the dendrimer ratio was demonstrated in experiments with BSA labeled with fluorescent markers. The fouling resistance of membranes prepared with 20 % PAMAM G0 was further investigated, by filtering oil in water emulsions, confirming their superior performance when compared with the pristine membranes.

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REFERENCES

- (1) He, Y.; Tang, Y. P.; Chung, T. S. Concurrent Removal of Selenium and Arsenic from Water Using Polyhedral Oligomeric Silsesquioxane (POSS)–Polyamide Thin-Film

Nanocomposite Nanofiltration Membranes. *Ind. Eng. Chem. Res.* **2016**, *55* (50), 12929-12938.

(2) Xie, W.; Geise, G. M.; Freeman, B. D.; Lee, H. S.; Byun, G.; McGrath, J. E. Polyamide interfacial composite membranes prepared from m-phenylene diamine, trimesoyl chloride and a new disulfonated diamine. *J. Membr. Sci.* **2012**, *403-404*, 152-161.

(3) Duong, P. H.; Chisca, S.; Hong, P. Y.; Cheng, H.; Nunes, S. P.; Chung, T. S. Hydroxyl Functionalized Polytriazole-co-polyoxadiazole as Substrates for Forward Osmosis Membranes. *ACS Appl. Mater. Interfaces* **2015**, *7* (7), 3960-73.

(4) Ren, J.; McCutcheon, J. R. A new commercial thin film composite membrane for forward osmosis. *Desalination* **2014**, *343* (0), 187-193.

(5) Chung, T.-S.; Luo, L.; Wan, C. F.; Cui, Y.; Amy, G. What is next for forward osmosis (FO) and pressure retarded osmosis (PRO). *Sep. Purif. Technol.* **2015**, *156*, 856-860.

(6) Valladares Linares, R.; Li, Z. Y.; Sarp, S.; Park, Y. G.; Amy, G.; Vrouwenvelder, J. S. Higher boron rejection with a new TFC forward osmosis membrane. *Desalination Water Treat.* **2015**, *55* (10), 2734-2740.

(7) Duong, P. H. H.; Nunes, S. P.; Chung, T.-S. Dual-skinned polyamide/poly(vinylidene fluoride)/cellulose acetate membranes with embedded woven. *J. Membr. Sci.* **2016**, *520*, 840-849.

(8) Zirehpour, A.; Rahimpour, A.; Ulbricht, M. Nano-sized metal organic framework to improve the structural properties and desalination performance of thin film composite forward osmosis membrane. *J. Membr. Sci.* **2017**, *531*, 59-67.

(9) Duong, P. H. H.; Chung, T. S. Application of thin film composite membranes with forward osmosis technology for the separation of emulsified oil-water. *J. Membr. Sci.* **2014**, *452* (0), 117-126.

- (10) Karan, S.; Jiang, Z.; Livingston, A. G. Sub-10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation. *Science* **2015**, *348* (6241), 1347-1351.
- (11) Veríssimo, S.; Peinemann, K. V.; Bordado, J. Influence of the diamine structure on the nanofiltration performance, surface morphology and surface charge of the composite polyamide membranes. *J. Membr. Sci.* **2006**, *279* (1), 266-275.
- (12) Kim, S. H.; Kwak, S. Y.; Suzuki, T. Positron annihilation spectroscopic evidence to demonstrate the flux-enhancement mechanism in morphology-controlled thin-film-composite (TFC) membrane. *Environ. Sci. Technol.* **2005**, *39* (6), 1764-1770.
- (13) Shen, L.; Zuo, J.; Wang, Y. Tris(2-aminoethyl)amine in-situ modified thin-film composite membranes for forward osmosis applications. *J. Membr. Sci.* **2017**, *537*, 186-201.
- (14) Duong, P. H. H.; Hong, P.-Y.; Musteata, V.; Peinemann, K. V.; Nunes, S. P. Thin Film Polyamide Membranes with Photoresponsive Antibacterial Activity. *ChemistrySelect* **2017**, *2* (22), 6612-6616.
- (15) Ma, D.; Peh, S. B.; Han, G.; Chen, S. B. Thin-Film Nanocomposite (TFN) Membranes Incorporated with Super-Hydrophilic Metal–Organic Framework (MOF) UiO-66: Toward Enhancement of Water Flux and Salt Rejection. *ACS Appl. Mater. Interfaces* **2017**, *9* (8), 7523-7534.
- (16) Song, X.; Zhou, Q.; Zhang, T.; Xu, H.; Wang, Z. Pressure-assisted preparation of graphene oxide quantum dot-incorporated reverse osmosis membranes: Antifouling and chlorine resistance potentials. *J. Mater. Chem. A* **2016**, *4* (43), 16896-16905.
- (17) Perreault, F.; Tousley, M. E.; Elimelech, M. Thin-Film Composite Polyamide Membranes Functionalized with Biocidal Graphene Oxide Nanosheets. *Environ. Sci. Technol. Lett.* **2014**, *1* (1), 71-76.

- (18) Huang, X.; Marsh, K. L.; McVerry, B. T.; Hoek, E. M. V.; Kaner, R. B. Low-Fouling Antibacterial Reverse Osmosis Membranes via Surface Grafting of Graphene Oxide. *ACS Appl. Mater. Interfaces* **2016**, 8 (23), 14334-14338.
- (19) Shen, L.; Zhang, X.; Zuo, J.; Wang, Y. Performance enhancement of TFC FO membranes with polyethyleneimine modification and post-treatment. *J. Membr. Sci.* **2017**, 534, 46-58.
- (20) Marré Tirado, M. L.; Bass, M.; Piatkovsky, M.; Ulbricht, M.; Herzberg, M.; Freger, V. Assessing biofouling resistance of a polyamide reverse osmosis membrane surface-modified with a zwitterionic polymer. *J. Membr. Sci.* **2016**, 520, 490-498.
- (21) Kasemset, S.; Lee, A.; Miller, D. J.; Freeman, B. D.; Sharma, M. M. Effect of polydopamine deposition conditions on fouling resistance, physical properties, and permeation properties of reverse osmosis membranes in oil/water separation. *J. Membr. Sci.* **2013**, 425, 208-216.
- (22) Baek, Y.; Freeman, B. D.; Zydney, A. L.; Yoon, J. A Facile Surface Modification for Antifouling Reverse Osmosis Membranes Using Polydopamine under UV Irradiation. *Ind. Eng. Chem. Res.* **2017**, 56 (19), 5756-5760.
- (23) Nikkola, J.; Sievänen, J.; Raulio, M.; Wei, J.; Vuorinen, J.; Tang, C. Y. Surface modification of thin film composite polyamide membrane using atomic layer deposition method. *J. Membr. Sci.* **2014**, 450, 174-180.
- (24) Reis, R.; Dumée, L. F.; He, L.; She, F.; Orbell, J. D.; Winther-Jensen, B.; Duke, M. C. Amine Enrichment of Thin-Film Composite Membranes via Low Pressure Plasma Polymerization for Antimicrobial Adhesion. *ACS Appl. Mater. Interfaces* **2015**, 7 (27), 14644-14653.

- (25) Reis, R.; Dumée, L. F.; Tardy, B. L.; Dagastine, R.; Orbell, J. D.; Schutz, J. A.; Duke, M. C. Towards Enhanced Performance Thin-film Composite Membranes via Surface Plasma Modification. *Sci. Rep.* **2016**, *6*.
- (26) Grayson, S. M.; Fréchet, J. M. J. Convergent Dendrons and Dendrimers: from Synthesis to Applications. *Chem. Rev.* **2001**, *101* (12), 3819-3868.
- (27) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. A New Class of Polymers: Starburst-Dendritic Macromolecules. *Polym. J.* **1985**, *17* (1), 117-132.
- (28) Gillies, E. R.; Fréchet, J. M. J. Dendrimers and dendritic polymers in drug delivery. *Drug Discov. Today* **2005**, *10* (1), 35-43.
- (29) Esfand, R.; Tomalia, D. A. Poly(amidoamine) (PAMAM) dendrimers: from biomimicry to drug delivery and biomedical applications. *Drug Discov. Today* **2001**, *6* (8), 427-436.
- (30) Lee, C. C.; MacKay, J. A.; Frechet, J. M. J.; Szoka, F. C. Designing dendrimers for biological applications. *Nat Biotech* **2005**, *23* (12), 1517-1526.
- (31) Helms, B.; Fréchet, J. M. J. The Dendrimer Effect in Homogeneous Catalysis. *Adv. Synth. Catal.* **2006**, *348* (10-11), 1125-1148.
- (32) Borisova, B.; Sánchez, A.; Jiménez-Falcao, S.; Martín, M.; Salazar, P.; Parrado, C.; Pingarrón, J. M.; Villalonga, R. Reduced graphene oxide-carboxymethylcellulose layered with platinum nanoparticles/PAMAM dendrimer/magnetic nanoparticles hybrids. Application to the preparation of enzyme electrochemical biosensors. *Sensors Actuators B: Chem.* **2016**, *232*, 84-90.
- (33) Sousa, M. A. M.; Siqueira, J. R.; Vercik, A.; Schöning, M. J.; Oliveira, O. N. Determining the Optimized Layer-by-Layer Film Architecture With Dendrimer/Carbon

Nanotubes for Field-Effect Sensors. *IEEE Sens. J.* **2017**, *17* (6), 1735-1740.

(34) Xiao, Y.; Chung, T. S.; Chng, M. L. Surface characterization, modification chemistry, and separation performance of polyimide and polyamidoamine dendrimer composite films.

Langmuir **2004**, *20* (19), 8230-8238.

(35) Kovvali, A. S.; Sirkar, K. K. Dendrimer Liquid Membranes: CO₂ Separation from Gas Mixtures. *Ind. Eng. Chem. Res.* **2001**, *40* (11), 2502-2511.

(36) Hayati, B.; Maleki, A.; Najafi, F.; Daraei, H.; Gharibi, F.; McKay, G. Synthesis and characterization of PAMAM/CNT nanocomposite as a super-capacity adsorbent for heavy metal (Ni²⁺, Zn²⁺, As³⁺, Co²⁺) removal from wastewater. *J. Mol. Liq.* **2016**, *224*, 1032-1040.

(37) Xiao, W.; Yan, B.; Zeng, H.; Liu, Q. Dendrimer functionalized graphene oxide for selenium removal. *Carbon* **2016**, *105*, 655-664.

(38) Jawor, A.; Hoek, E. M. V. Removing Cadmium Ions from Water via Nanoparticle-Enhanced Ultrafiltration. *Environ. Sci. Technol.* **2010**, *44* (7), 2570-2576.

(39) Amariei, G.; Santiago-Morales, J.; Boltes, K.; Letón, P.; Iriepa, I.; Moraleda, I.; Fernández-Alba, A. R.; Rosal, R. Dendrimer-functionalized electrospun nanofibres as dual-action water treatment membranes. *Sci. Total Environ.* **2017**, *601*, 732-740.

(40) Zhu, W.-P.; Gao, J.; Sun, S.-P.; Zhang, S.; Chung, T.-S. Poly(amidoamine) dendrimer (PAMAM) grafted on thin film composite (TFC) nanofiltration (NF) hollow fiber membranes for heavy metal removal. *J. Membr. Sci.* **2015**, *487*, 117-126.

(41) Zuo, J.; Lai, J.-Y.; Chung, T.-S. In-situ synthesis and cross-linking of polyamide thin film composite (TFC) membranes for bioethanol applications. *J. Membr. Sci.* **2014**, *458*, 47-57.

(42) Kanchi, S.; Suresh, G.; Priyakumar, U. D.; Ayappa, K. G.; Maiti, P. K. Molecular Dynamics Study of the Structure, Flexibility, and Hydrophilicity of PETIM Dendrimers: A

Comparison with PAMAM Dendrimers. *The Journal of Physical Chemistry B* **2015**, *119* (41), 12990-13001.

(43) Anwand, D.; Müller, F. W.; Strehmel, B.; Schiller, K. Determination of the molecular mobility and the free volume of thin polymeric films with fluorescence probes. *Makromol. Chem.* **1991**, *192*, 1981-1991.

(44) Chen, H.; Hung, W.-S.; Lo, C.-H.; Huang, S.-H.; Cheng, M.-L.; Liu, G.; Lee, K.-R.; Lai, J.-Y.; Sun, Y.-M.; Hu, C.-C.; Suzuki, R.; Ohdaira, T.; Oshima, N.; Jean, Y. C. Free-Volume Depth Profile of Polymeric Membranes Studied by Positron Annihilation Spectroscopy: Layer Structure from Interfacial Polymerization. *Macromolecules* **2007**, *40* (21), 7542-7557.

(45) Fujioka, T.; Oshima, N.; Suzuki, R.; Price, W. E.; Nghiem, L. D. Probing the internal structure of reverse osmosis membranes by positron annihilation spectroscopy: Gaining more insight into the transport of water and small solutes. *J. Membr. Sci.* **2015**, *486*, 106-118.

(46) Kim, S.-J.; Kook, S.; O'Rourke, B. E.; Lee, J.; Hwang, M.; Kobayashi, Y.; Suzuki, R.; Kim, I. S. Characterization of pore size distribution (PSD) in cellulose triacetate (CTA) and polyamide (PA) thin active layers by positron annihilation lifetime spectroscopy (PALS) and fractional rejection (FR) method. *J. Membr. Sci.* **2017**, *527*, 143-151.

(47) Zuo, J.; Chung, T.-S. Design and synthesis of a fluoro-silane amine monomer for novel thin film composite membranes to dehydrate ethanol via pervaporation. *J. Mater. Chem. A* **2013**, *1* (34), 9814-9826.

(48) Le, N. L.; Bettahalli, N. M. S.; Nunes, S. P.; Chung, T.-S. Outer-selective thin film composite (TFC) hollow fiber membranes for osmotic power generation. *J. Membr. Sci.* **2016**, *505*, 157-166.

(49) An, Q.-F.; Ji, Y.-L.; Hung, W.-S.; Lee, K.-R.; Gao, C.-J. AMOC Positron Annihilation

Study of Zwitterionic Nanofiltration Membranes: Correlation between Fine Structure and Ultrahigh Permeability. *Macromolecules* **2013**, *46* (6), 2228-2234.

(50) Duong, P. H. H.; Zuo, J.; Chung, T.-S. Highly crosslinked layer-by-layer polyelectrolyte FO membranes: Understanding effects of salt concentration and deposition time on FO performance. *J. Membr. Sci.* **2013**, *427*, 411-421.

(51) Tung, K.-L.; Jean, Y.-C.; Nanda, D.; Lee, K.-R.; Hung, W.-S.; Lo, C.-H.; Lai, J.-Y. Characterization of multilayer nanofiltration membranes using positron annihilation spectroscopy. *J. Membr. Sci.* **2009**, *343* (1), 147-156.

(52) Shen, L.; Zuo, J.; Wang, Y. Tris(2-aminoethyl)amine in-situ modified thin-film composite membranes for forward osmosis applications. *J. Membr. Sci.* **2017**, *537* (Supplement C), 186-201.

(53) Ren, J.; McCutcheon, J. R. A new commercial thin film composite membrane for forward osmosis. *Desalination* **2014**, *343* (Supplement C), 187-193.

(54) Han, G.; Zhao, B.; Fu, F.; Chung, T.-S.; Weber, M.; Staudt, C.; Maletzko, C. High performance thin-film composite membranes with mesh-reinforced hydrophilic sulfonated polyphenylenesulfone (sPPSU) substrates for osmotically driven processes. *J. Membr. Sci.* **2016**, *502* (Supplement C), 84-93.

(55) Zhang, X.; Tian, J.; Ren, Z.; Shi, W.; Zhang, Z.; Xu, Y.; Gao, S.; Cui, F. High performance thin-film composite (TFC) forward osmosis (FO) membrane fabricated on novel hydrophilic disulfonated poly(arylene ether sulfone) multiblock copolymer/polysulfone substrate. *J. Membr. Sci.* **2016**, *520* (Supplement C), 529-539.

(56) Ghanbari, M.; Emadzadeh, D.; Lau, W. J.; Riazi, H.; Almasi, D.; Ismail, A. F. Minimizing structural parameter of thin film composite forward osmosis membranes using

1
2
3 polysulfone/halloysite nanotubes as membrane substrates. *Desalination* **2016**, 377 (Supplement
4
5 C), 152-162.
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8
9
10
11
12
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14
15
16
17
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19
20
21
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23
24
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