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**From micro to nano: Polyamide thin film on microfiltration ceramic
tubular membranes for nanofiltration**

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Research Highlights:

1. PEI-based polyamide thin film was synthesized on microfiltration ceramic tubular membranes without an intermediate layer.
2. The membranes demonstrated excellent nanofiltration performance with a PWP of 16-18 LMH bar⁻¹ and a MWCO of ~250 Da.
3. The membranes also showed good divalent salt rejections for CaCl₂, MgCl₂ and MgSO₄.
4. The rejections of MgCl₂ and sucrose remained high at elevated temperature of 80 °C.
5. The mechanical property of the polyamide film was studied using the AFM pinpoint mode and the modulus was measured.

Abstracts:

Interfacial polymerization is an effective technique to synthesize high performance polyamide thin film membranes. However, it is still very challenging to apply this technique on ceramic hollow fibres or tubular membranes, especially when the substrate pore size is in the microfiltration range. In this study, we demonstrated that thin polyamide layer can be synthesized directly on microfiltration ceramic tubular membranes with a surface pore size of 0.1-0.2 microns via interfacial polymerization without an intermediate layer. A thin polyamide layer with a thickness 30-40 nm was coated on the inner surface of the ceramic substrate by circulating the monomers of branched polyethyleneimine (PEI), piperazine (PIP), and trimesoyl chloride (TMC) through the membrane lumen. The thin film layer showed good integration with the ceramic substrate and could withstand high pressure of at least 10 bar. The mechanical property of the polyamide layer was examined using AFM and the modulus was measured. The thin film composite membranes demonstrated excellent nanofiltration performance with a pure water permeability of 16-18 LMH bar⁻¹ and a molecular weight cut-off of ~250 Da. The membranes also showed good salt rejections (>90%) to CaCl₂, MgCl₂ and MgSO₄, and still maintained high rejections of MgCl₂ and sucrose at elevated temperature of 80 °C. The use of highly inert ceramic substrates has enabled the application of polyamide membranes under more challenging conditions.

Keywords:

Interfacial polymerization, Polyamide thin film, Ceramic membranes, Nanofiltration

Graphical Abstract:

1. Introduction

Nanofiltration has emerged as an important membrane process for water softening, wastewater treatment, pharmaceutical processing and food production [1-3]. It can be operated at a lower pressure compared to reverse osmosis as nanofiltration membranes generally have a less dense structure or a larger pore size, and the separation process is seldom restricted by osmotic pressure. With a molecular weight cut-off (MWCO) between 200 and 1000 Da by definition, nanofiltration membranes can effectively separate small organic molecules and various inorganic salts [4, 5]. The rejection of solutes is primarily based on size exclusion as well as electrostatic interaction. Though having a low rejection of monovalent ions, nanofiltration membranes exhibit a high rejection of multivalent ions such as Mg^{2+} and Ca^{2+} .

Thin film composite (TFC) membranes composed of a thin selective layer and a strong support are widely used for nanofiltration [6]. Compared to integrally skinned asymmetric membranes which have a skin layer on top of a more porous support layer of the same material, TFC membranes generally have a higher permeability as the thin selective layer can be optimized separately [7]. Various materials have been explored for the selective layer of TFC membranes, for example polyamide, polymer of intrinsic microporosity, graphene oxide, metal organic frameworks and etc. [8-11] Among them, polyamide thin film is one of the most widely used TFC membranes due to the high permeability, excellent chemical resistance and mechanical robustness [7, 12] Polyamide thin film membranes have been synthesized using interfacial polymerization, a promising approach for large-scale production of high performance TFC membranes [13-15]. Flat sheet polyamide TFC membranes are now commercially produced by companies like Dow Filmtec, GE Osmonics and Nitto-Denko [7].

The polyamide thin layer is commonly formed on a porous polymeric substrate, primarily ultrafiltration membranes. Many studies have been focusing on the synthesis of the polyamide layers for enhanced membrane performance, which is strongly dependent on the thin film thickness, structure and morphology [16-18]. Ultrathin polyamide layers with a sub-10 nm thickness were shown to have an ultrahigh permeability [16]. The crumple and Turing structures of polyamide layers with a high surface roughness could also improve the permeability of the membranes [16, 17]. In addition, the surface charge of the polyamide layer was altered to enhance salt rejection rates as positively charged membranes could reject divalent metal ions through electrostatic repulsion in addition to size exclusion [19]. Besides

the separating layer, many recent studies have revealed the importance of substrates in determining the performance of polyamide TFC membranes [20, 21]. An increase in substrate surface porosity can improve the permeability of the TFC membrane through shortened effective diffusion paths of permeating species.

As the applications of polyamide membranes have been further extended for more challenging conditions involving organic solvents, wide pH range and high temperature [12, 22, 23], the substrates used for TFC membranes have to be considered more carefully. Polysulfone ultrafiltration membranes are one of the most commonly used substrates for commercial polyamide membranes but they are not very solvent **resistant** and many commercial membranes have a maximum operating temperature of 50 °C [14]. Polymeric substrates with a strong chemical or/and thermal resistance such as polyimide, polyacrylonitrile, poly(ether ether ketone) and poly (m-phenylene isophthalamide) have been studied for organic solvent or high temperature nanofiltration [24-26]. However, substrate pretreatments such as chemical cross-linking are usually necessary to improve the chemical stability of polymeric substrates, which may in turn result in a significant reduction in permeability. Recently, inorganic substrates such as ceramic hollow fibre and tubular membranes have been studied as alternative and more versatile substrates for polyamide thin film membranes [27-29]. With high chemical, thermal and mechanical stabilities, polyamide thin film on ceramic substrates could potentially be used in applications with more challenging conditions. And the hollow fibre or tubular geometry could improve the scalability of the composite membranes.

However, there are a number of constraints for using ceramic hollow fibres and tubular membranes as the substrates for constructing polyamide TFC membranes. During the polyamide thin film synthesis, the aqueous solution reactants are first introduced to the substrate surface before contacting with the organic phase reactants. The pore size, surface roughness and hydrophilicity of the substrates could affect the thin film formation [13, 30]. Unfortunately, most of the ceramic substrates with low production cost normally have relatively large pore sizes (in micron range), which cause the difficulty in creating a stable aqueous-organic interface for the interfacial polymerization reaction to take place. To overcome the challenge, an intermediate layer was normally coated on the substrates before the synthesis of a polyamide layer. Materials such as γ -alumina, titanium oxide, polydopamine and polyethyleneimine have previously been applied as the intermediate layer, which aimed to reduce the surface pore size (<10 nm) or to improve the hydrophilicity of the substrates [27,

29, 31]. On the other hand, the introduction of the intermediate layer added an extra step in the membrane fabrication process and the coating of ceramic nanoparticles required an additional sintering step. Without an intermediate layer, the ceramic substrates should possess relatively small pore sizes. For instant, Xia et al. successfully synthesized a polyamide layer on ultrafiltration ceramic substrates with a pore size of 30 nm [28]. However, since there are many commercial microfiltration ceramic membranes available in the market [32], it is of great interest to use these substrates directly for polyamide thin film synthesis without any complex pre-treatment, though it is a challenging task. The use of microfiltration ceramic substrates would also mitigate mass transfer resistance of the composite membranes.

In this study, we chose commercial ceramic tubular membranes with pore sizes of 100 and 200 nm as the substrates to synthesize polyamide thin film membranes. The polyamide film was synthesized directly on the ceramic substrate without an intermediate layer via interfacial polymerization using commonly used monomers [33]. The aqueous and organic phase reactants were introduced to the inner surface of the substrates through circulation in a controlled manner to ensure the formation of a perfect polyamide layer on the substrate. The polyamide films were characterized using a series of instruments. Among them, the atomic force microscopy (AFM) pinpoint mode was highlighted in this study as it allowed us to study the mechanical property of the thin film on the substrates directly. The resultant polyamide-ceramic composite membranes were tested for nanofiltration application to retain various salts, dyes and sugars. To demonstrate the advantage of ceramic substrates, the polyamide composite membranes were also tested for high temperature nanofiltration at temperature 50-80 °C, where many polymeric substrates may undergo severe swelling. This study not only showed the versatility of polyamide membranes on ceramic substrates, but also demonstrated the potential use of commonly available microfiltration ceramic tubular membranes for value-added applications.

2. Experimental

2.1. Materials

Ceramic tubular membranes with pore sizes of 100 and 200 nm were supplied by Coorstek Netherlands BV. The alumina substrates with an outer diameter of 5 mm and an inner diameter of 3 mm were cut into 10 cm in length for polyamide thin film synthesis. Branched

polyethyleneimine (PEI) with molecular weights 50,000–100,000 g/mol (30 wt% in aqueous solution, Polyscience), piperazine (PIP, 99 %, Merck), trimesoyl chloride (TMC, 98 %, Sigma-Aldrich), and cyclohexane (99.5 %, Merck) were used for interfacial polymerization. All chemicals were used as received.

Polyethylene glycols (PEGs) with average molecular weights of 200, 300, 400, 600, 1000 g/mol and diethylene glycol ($M_w = 106.12$ g/mol) were used to determine the molecular weight cut-off (MWCO) of the membranes. A series of neutral solutes including glucose, sucrose and raffinose (Merck), dyes including methyl orange, fuschin acid and rose begal (Sigma Aldrich) and different analytical grade salts including CaCl_2 , MgCl_2 , MgSO_4 , Na_2SO_4 and NaCl (Merck) were used in the preparation of feed solutions for membrane performance tests. Deionized water (Milli-Q, 18 $M\Omega$ cm) was used for the aqueous solutions preparation.

2.2. Preparation of polyamide layer

An aqueous solution containing 0.25 wt% PEI and 0.1 wt% PIP was first prepared. The solution was stirred for 2 hours prior to the interfacial polymerization synthesis. Ceramic tubular membranes with 2 different pore sizes, 100 and 200 nm were used as the substrates. During the membrane synthesis, the aqueous solution was introduced into the lumen of the tubular substrates using a syringe. The substrates were left in contact with the solution for 30 min. After that, the excess aqueous solution was washed off by purging the lumen with cyclohexane using a peristaltic pump at a flow rate of 60 ml min^{-1} for 120 s. Then, the organic phase reactant containing 0.13 wt% TMC in cyclohexane was pumped through the lumen of the ceramic substrates at a flow rate of 15 ml min^{-1} for 120 s for the interfacial polymerization reaction to take place. The lumen with the synthesized polyamide layer was rinsed with DI water and then dried in the air overnight for further use.

2.3. Membrane characterization

The morphology of the membranes was examined using scanning electron microscope (SEM, Zeiss EVO 50, Carl Zeiss AG, Germany). X-ray photoelectron spectroscopy (XPS) analysis was conducted to study the formation of the polyamide layer using a Kratos Axis Supra spectrophotometer equipped with a dual anode monochromatic $K\alpha$ excitation source. The pore

size and the pore size distribution of the ceramic substrates were determined by a capillary flow porometer (CFP 1500A, Porous Material. Inc., USA). Iso-butanol was used as the wetting liquid and nitrogen was used as the displacement gas during the measurement. The membrane surface charge at varied pH was measured by streaming potential method using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) where 0.1 M sodium chloride was used as the electrolyte solution. An inert PTFE rod was inserted in the lumen of all membrane samples to achieve a low electrolyte flow rate required during the measurement.

Atomic force microscopy (AFM) measurement (Park NX10) was used to study the surface topology, roughness as well as the mechanical strength of the polyamide thin film layer on the ceramic substrates. The non-contact mode was used to study the surface topology while the pinpoint mode was used to study the mechanical properties. During the pinpoint mode scan, force-distance curves across a scanning area were obtained and the modulus at each measuring point was calculated. A total of 256 x 256 points were measured for a scan area of 5 x 5 μm and the moduli across the scanned area were illustrated in a 2D image.

2.4 Nanofiltration performance tests

The pure water permeation of the prepared membranes was measured in a cross-flow mode. Pure water was circulated through the lumen of the membranes at a flow rate of 150 ml min^{-1} and an effective transmembrane pressure 2 bar. The membrane was allowed to undergo compaction for at least 1 hour before the steady state permeation flux was measured. **At least 3 membrane samples were tested to obtain an average water permeation flux.** The pure water permeation was also conducted at a higher transmembrane pressure, up to 10 bar to study the mechanical strength of the coating layer on the substrates. The pure water permeability, PWP ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$) was calculated using the equation:

$$PWP = \frac{F}{\Delta P} = \frac{Q}{A\Delta P} \quad (1)$$

where F is the permeation flux ($\text{L m}^{-2} \text{h}^{-1}$), ΔP is the transmembrane pressure (bar), Q is the volumetric permeation flow rate (L h^{-1}) and A is the effective membrane area (m^2).

PEGs and diethylene glycol were used to determine the MWCO of the membranes. PEGs and diethylene glycol solutions with a concentration of 1000 ppm were fed to the membrane module at 2 bar during the test. The concentration of the permeate was measured using Agilent

1260 Infinity GPC. The membranes were also tested for sugar and dye rejections using glucose, sucrose, raffinose, methyl orange, acid fuschin and rose begal. **Solutions with a single solute were used in the rejection tests**, and the feed concentrations of the sugar and dye solutions were 1000 and 20 ppm, respectively. Various salts including CaCl_2 , MgCl_2 , MgSO_4 , Na_2SO_4 and NaCl were used to study the desalination performance of the membranes. The membranes were tested at 2 bar for salt concentration of 1000 ppm and at 4 bar for salt concentration of 2000 ppm. The solute rejection, R (%) was calculated using the equation:

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (2)$$

where C_f and C_p are the solute concentrations (ppm) in the feed and permeate solutions, respectively.

The polyamide ceramic composite membranes were also tested for high temperature nanofiltration where MgCl_2 , MgSO_4 , sucrose and PEG-300 were used as the solutes. The feed solutions with a concentration of 1000 ppm were heated in a heating jacket tank, and then fed to the membrane module. Starting from room temperature, the temperature was subsequently increased to 50, 60, 70 and 80 °C. The tests were run for at least 3 hours at each temperature and permeate samples were collected hourly. In addition, a slightly longer term experiment was also conducted at 70 °C to study the thermal stability of the composite membrane. 1000 ppm of MgCl_2 was used as the feed solution and the membrane was tested for 4 cycles with a total time of 48 hours. The filtration test was run for 12 hours in each cycle, and the membrane was cooled to room temperature and stored in water between cycles.

3. Results and discussions

3.1. Formation of polyamide membrane on ceramic tubular substrates

Microfiltration ceramic tubular membranes were used as the substrates for synthesizing polyamide thin film membranes as they are commercially available at low cost. With high porosity and water permeability, the microfiltration substrates will contribute a low mass transfer resistance to the thin film composite membranes. Figure 1a shows the SEM image **of** the cross section of the tubular membranes. The membranes used in this study had an average inner and outer diameter of 3 and 5 mm, respectively. Figure 1b is the cross section image near

the inner surface of the substrate. It can be seen that the substrate consists of two layers: a support layer with large ceramic particles that provides strong mechanical properties, and a surface layer with smaller particles that provides a smoother surface and a more homogeneous pore size. The ceramic membranes with two pore sizes, 100 and 200 nm (denoted as S-100 and S-200) were used in this study and both substrates had a fairly sharp pore size distribution (Figure 1c). The mean pore sizes of the substrates S-100 and S-200 were 127 and 195 nm, respectively. The substrates had much larger pore sizes compared to the ceramic substrates used in previous studies for polyamide thin film synthesis [27, 28]. Figure 1d and e show the surface morphology of the ceramic substrates, and it was observed that the substrates S-200 had a much porous surface structure compared to the substrates S-100.

Figure 1: SEM images of the cross-section of the ceramic substrate S-100: (a) overall view and (b) near the inner surface. (c) Pore size distribution of the ceramic substrates obtained using the gas-liquid porometry. SEM images of surface morphology of ceramic substrate (d) S-100 and (e) S-200.

A PEI-based polyamide membrane was successfully synthesized on the inner surface of the ceramic substrates via interfacial polymerization. Figure 2a and b show the SEM images of the surface of the synthesized polyamide layers, PA-100 and PA-200 on the ceramic substrates S-

100 and S-200, respectively. The polyamide layers formed were relatively smooth compared to those synthesized using m-phenylene diamine (MPD) as the aqueous monomer where crumpled structure was normally observed [28, 30]. The smooth surface morphology is commonly observed when monomers like PEI and PIP are used [19, 34]. In both of the membranes, the film was coated around the ceramic particles on the substrate surface and the morphology of the ceramic substrate underneath could still be seen clearly. Since there is no strong chemical bond formed between the two materials, the formation of thin film around the particles may enhance their integration. Figure 2c and d show the cross-section of the membranes. The polyamide layers had a thickness of about 30-40 nm for both membranes PA-100 and PA-200. The polyamide layer synthesized was relatively thin compared to previous studies that used the similar circulation method, which could be due to the more extensive washing step in this study [28, 34]. It can also be seen from the cross-sectional view that the polyamide films formed around the top surface of ceramic particles. Unlike what observed in the study by Sing et al. [35], no penetration of polyamide into the pores was observed though the pore size of the substrates was in the microfiltration range.

Figure 2: SEM images of the surface and the cross-section of the polyamide thin film composite membranes (a, c) PA-100 and (b, d) PA-200.

Figure 3 shows the AFM images of the topographies of the ceramic substrates and the polyamide thin films. The root-mean-square surface roughness of the substrates S-100 and S-200 were 48.3 and 68.6 nm, respectively. The higher surface roughness of S-200 was contributed by the more porous surface morphology. Overall, the surface roughness of both of the substrates was relatively smooth as microfiltration ceramic substrates could have surface roughness larger than 100 nm [29, 36]. The smaller surface roughness was favourable for synthesis of thin film membranes [37]. After the coating of a polyamide layer, the surface became smoother with a surface roughness of 28.0 and 34.3 nm for PA-100 and PA-200, respectively. The surface roughness of both membranes was closer after the coating as similar surface morphology was obtained from the interfacial polymerization. The low surface roughness was also consistent with previous studies on PEI-based polyamide membranes [29, 34].

Figure 3: AFM topography scan images of (a, c) the ceramic substrates and (b, d) the polyamide thin films.

The chemical composition of the thin film composite membranes was analysed using XPS, as shown in Figure 4a-c. From the wide scan spectrums, three major peaks were observed for the alumina substrates at 531.4, 119.4 and 74.4 eV, which corresponded to O1s, Al2s and Al2p, respectively. When the polyamide layer was coated on the ceramic surface, the peaks corresponded to Al were no longer observed while the peaks for nitrogen and carbon became obvious. The C1s peak of the polyamide layer from the narrow scan was deconvoluted in three peaks as follows: 283.6 eV corresponded to C-C and C-H bonds, 286.0 eV corresponded to C-N bond, and 287.6 eV corresponded to C-C=O and N-C=O bonds [38]. The O1s peak of the polyamide layer was deconvoluted in two peaks: 531.7 and 533.1 which correspond to N-C=O and C-C=O bonds, respectively. The cross-linking between the monomers can be confirmed by the N-C=O peak in the deconvoluted C1s and O1s peaks, where the chloride groups (Cl-C=O) of TMC were bonded to the -NH₂ groups of PEI and PIP. Figure 4d shows the interfacial polymerization reaction and the possible PEI-based polyamide structure. As the PEI used in this study had a high molecular weight and was also highly branched, the “pore structure” formed in the polyamide layer could be looser than those synthesized using monomers like MPD or PIP. A small amount of PIP was added in this study as it could improve the cross-linking and form a denser PEI-based polyamide layer.

Figure 4: XPS spectra of ceramic substrates and polyamide layer: (a) Wide scan spectra of (i) S-100 (ii) S-200 (iii) PA-100 (iv) PA-200. Narrow scan results of polyamide membranes: (b) C1s and (c) O1s peak. (d) Reaction schematic between PEI+PIP and TMC, and the possible structure of the PEI-based polyamide network.

The success of polyamide thin film synthesis on microfiltration ceramic substrate was highly dependent on the formation of stable aqueous-organic interface during the synthesis process. Figure 5 illustrates the liquid interface and the formation of polyamide layer on the ceramic substrates. The ceramic substrates used in this study were highly hydrophilic, and water droplet was absorbed into the substrates in less than 1 s when tested for the water contact angle. When the aqueous phase reactant was introduced to the lumen of the ceramic substrate, the solution was expected to wet the surface and fill up the pores of the substrates quickly. Washing off the excess aqueous solution was an important step and cyclohexane was used for washing as it was also the solvent for the organic phase reactant. Compared to air-purging and atmospheric drying [27, 28], the solvent washing method was easier to control and was also in a same manner of how the organic reactant was introduced after that. The cyclohexane flow pushed the aqueous-organic liquid interface close to the substrate surface, so that the polyamide layer will form right on the substrate. As the ceramic substrates were highly hydrophilic, the meniscus of the aqueous solution should be concave at the substrate pore entrances [30]. Therefore, the polyamide film synthesized was slightly below the substrate surface at the pores, forming a layer around the ceramic particles. Besides, PEI in the aqueous solution may adsorb on the –OH group rich ceramic surface, which could help the formation of continuous polyamide layer on the substrates [29].

Figure 5: Illustration of the formation of polyamide layer at the liquid interface on the substrate surface.

3.2. Mechanical properties of polyamide thin film on ceramic tubular substrates

The study of the mechanical properties of the polyamide layer on the ceramic substrates is important because the pore size of the substrates used was relatively large, in the microfiltration range. Besides the challenges for synthesis, thin films on substrates with a large pore size could experience a higher stress during pressure-driven applications. The pinpoint technique on AFM was used to determine the elastic modulus of the polyamide membranes on the ceramic substrates. Figure 6a and b show the moduli of the membranes measured across the scan area. The patterns look different compared to the topography images shown in the previous section (Figure 3b and d). Especially for PA-200, the area with high moduli is very distinct from the area with low moduli. The mean moduli obtained were 5.11 and 3.95 GPa for membrane PA-100 and PA-200, respectively, and these values were higher than the modulus of commercial polyamide nylon [39]. The moduli were also higher than that measured using the wrinkling-cracking method, where one of the highest modulus values measured was only 2.71 GPa [16]. The high moduli measured in this study could be contributed by the ceramic substrates underneath the polyamide layer, and further analysis on the measured data was required to determine the real modulus of the polyamide layer.

Figure 6c illustrates the AFM scanning on the polyamide surface. As it can be seen in the image, part of the polyamide film was intact with the ceramic particles but part of it was between the particles. For the areas that were right on top of the ceramic particles, the layer was well supported and could therefore withstand a higher force during the modulus measurement. However, the higher elastic modulus measured in those areas does not represent the real mechanical strength of the polyamide layer. And it is essential to measure the areas between the ceramic particles – the pore areas – and the modulus in those areas will be close to the intrinsic modulus of the polyamide layer. Also, these are weaker areas that are more prone to breakage during high pressure applications. Figure 6d shows an example of an AFM line scan result for both height and modulus. In the height scan result, the peaks were from the ceramic particles while the valleys were the pore areas. As predicted, the modulus obtained followed the same pattern as the height, where the valleys in the height scan also had a low modulus. This confirmed that the smaller modulus measured was from the pore areas and the value would be closer to the real modulus value of the thin film.

Figure 6: (a, b) Modulus of the polyamide layer of membranes PA-100 and PA-200 obtained from the AFM pin-point scan. (c) Illustration of the AFM scan on the surface of the

polyamide layer on ceramic substrates. (d) Example of a line scan result showing the change in height and modulus across the membrane.

All the modulus data measured were extracted and plotted in a distribution curve, as shown in Figure 7. For both membranes PA-100 and PA-200, a bimodal distribution was observed with one peak below 2 GPa and another one above. The distribution below 2 GPa could be contributed by the pore areas where the modulus was lower, while the distribution above 2 GPa could be contributed by the area where the polyamide was sitting on the ceramic particles. However, the modulus distribution of both of the samples was very different at the pore areas, and the membrane PA-200 had a larger distribution in that region. This could be due to the more porous surface morphology of the substrate S-200 and a larger area of the film was at the pore areas. The peaked modulus of PA-200 was at 0.55 ± 0.5 GPa, which was lower than PA-100 at 0.90 ± 0.5 GPa. The smaller modulus of PA-200 could be due to the long stretch of polymer at the pore entrances (between the ceramic particles), but may also be closer to the intrinsic value of the polyamide layer synthesized. While at the substrate area where the moduli were larger than 2 GPa, both membranes showed very similar distribution as the ceramic substrates could have affected the mechanical property of the polyamide layers in a similar manner. The pinpoint technique is a very useful tool to study the mechanical strength of thin film composite membranes especially for hollow fibre and tubular membranes. To the best of our knowledge, this is the first time that the modulus of the polyamide film on hollow fibres or tubular membranes is reported. Besides the simple sample preparation, this method also allows us to study the local mechanical property, which is more relevant to membrane applications.

Figure 7: Modulus distribution of the PA layer across the scan area: a bimodal distribution was observed in both membranes PA-100 and PA-200. Insert: Close-up of the distribution at modulus smaller than 2 GPa.

The mechanical strength of the polyamide composite membranes was further tested in pressure driven filtration tests. During the test, the transmembrane pressure in the cross-flow system was increased from 2 bar to 4, 6 and 10 bar and then back to 2 bar in a reverse order. At each pressure, the permeation test was run for at least 1 hour before the permeation flux was recorded. The permeation water flux of both membranes is shown in Figure 8. The increase of the water permeation flux was generally in a linear relationship with the increase of pressure. A slight membrane compaction was observed where the PWP dropped from 17.3 to 15.4 LMH bar⁻¹ for membrane PA-100, and from 19.1 to 18.2 LMH bar⁻¹ for membrane PA-200 when the pressure was increased from 2 to 10 bar. However, the permeability was recovered slightly and increased to 17.0 and 18.4 LMH bar⁻¹ for membranes PA-100 and PA-200, respectively, when the pressure was decreased to 2 bar at the end of the test. Even though substrates with a relatively large pore size were used in this study, the polyamide layers could still withstand high pressure at 10 bar. Ceramic substrates with a small pore size were used in previous studies, that could be mainly due to the challenges in the thin film synthesis. Polyamide is a strong material and the thin film membranes were previously tested at pressure up to 50 bar on substrates with a pore size of larger than 100 nm [16].

Figure 8: The water permeation of the polyamide membranes PA-100 and PA-200 at increasing and decreasing pressure.

3.3 Performance of polyamide-ceramic membranes in nanofiltration application

The PWP of the ceramic substrates and the polyamide composite membranes were tested in a cross-flow mode. The substrates S-100 and S-200 had a PWP of 589 ± 23 and 1069 ± 27 LMH bar^{-1} , respectively. The PWP of the substrates were moderately high compared to some ceramic membranes reported [40, 41], but were relatively high compared to many ultrafiltration polymeric substrates used for polyamide synthesis [34]. The microfiltration substrates used in this study should therefore contribute a low mass transfer resistance to the nanofiltration thin film membranes. The PWP of the polyamide membranes PA-100 and PA-200 were 16.7 ± 0.8 and 18.4 ± 0.7 LMH bar^{-1} , respectively. Both of the membranes exhibited similar water permeability though membranes PA-200 had a slightly higher permeability. The higher permeability could be attributed to the more porous substrates, as the surface porosity of the substrates was found affecting the water permeability in thin film composite membranes [20, 21]. The PWP of the membranes was considerably high compared to most polyamide membranes on hollow fibre and tubular membrane substrates [27, 42, 43], though it was slightly lower than some polyamide membranes synthesized using purely PEI monomers [29].

The incorporation of a small amount of PIP could have tightened the pore structure in the membranes, as shown in the MWCO result later on.

The MWCO of the polyamide composite ceramic membranes was tested with PEGs and diethylene glycol, and both of the membranes PA-100 and PA-200 had a similar MWCO of 240-260 Da, as shown in Figure 9. The membrane MWCO was smaller than most of the PEI-based polyamide membranes on hollow fibre or tubular membrane substrates [19, 29, 43]. Pure PEI-based polyamide membranes usually have MWCO between 350-500 Da and the addition of PIP in this study has shown effective in reducing the MWCO of the membranes without reducing the flux significantly. The PEG rejection of PA-200 was slightly lower than PA-100, which could be due to minor defects in the polyamide layer. The membrane PA-100 was also tested for sugar and dye rejections. The rejections of raffinose (504 g/mol), sucrose (342 g/mol) and glucose (180 g/mol) were 99.1, 98.9 and 87.4 %, respectively, and the rejections of rose bagel (875 g/mol), acid fuschin (586 g/mol) and methyl orange (327 g/mol) were 99.2, 99.9 and 99.0 %, respectively. The membranes showed versatility in rejecting various solutes in the nanofiltration range and could be useful to retain organic pollutants in wastewater.

Figure 9: Molecular weight cut-off of both PA-100 and PA-200 obtained using PEGs and diethylene glycol rejection tests. Sugar (glucose, sucrose and raffinose) and dye (methyl orange, acid fuschin and rose bengal) rejections of membrane PA-100 were also tested.

The membranes were also tested for salt rejection (Figure 10) and they showed good rejection for divalent ions with rejection >90%. For membrane PA-100, the rejections of CaCl_2 , MgCl_2 and MgSO_4 were 94.3, 95.2 and 91.6 %, respectively. However, the rejections of Na_2SO_4 and NaCl were only 65.3 and 36.4, respectively. The good rejection of divalent ion salts could be explained by the effect of steric hindrance as the hydrated radiuses of Mg^{2+} and Ca^{2+} are larger than Na^+ [44]. The same effect can also explain the higher rejection of Na_2SO_4 over NaCl as ion SO_4^{2-} has a larger hydrated radius. When tested using salt solution with a higher concentration 2000 ppm, the membrane still showed good rejection of MgCl_2 and MgSO_4 , with a rejection rate of 94.1 and 91.5 %, respectively. However, the consistently relatively lower MgSO_4 rejection compared to MgCl_2 at both feed concentrations could not be fully explained using the steric hindrance effect.

Figure 10: Performance of the polyamide-ceramic membranes in salt rejections. The salt rejection of both PA-100 and PA-200 membranes were tested using 1000 ppm of CaCl_2 , MgCl_2 , MgSO_4 , Na_2SO_4 and NaCl solutions. Higher salt concentration 2000 ppm of MgCl_2 , MgSO_4 were also tested using membrane PA-100.

To further understand the salt rejection results, the surface charge of the membranes were measured and the zeta potential results are presented in Figure 11. The zeta potential of the

tubular membrane was measured using the streaming potential method at pH ranging from 3 to 9.5. The ceramic substrate had an isoelectric point at about pH 5, exhibiting anionic surface charge under pH>5. However, the isoelectric points of both of the membrane PA-100 and PA-200 shifted significantly towards a higher pH but were not determined during the measurement due to the limited pH range of the equipment. Isoelectric points at a relatively high pH were observed previously when mixed PEI and PIP was used as the polyamide monomers [45]. The PEI-based polyamide membranes exhibited positively charged surface for a large pH range including at pH of the fed solution in this study (~pH 6.5). The positively charged surface was mainly attributed to the protonation of unreacted amine groups in the membranes. Therefore, the higher rejection of divalent ions could also be contributed by the Donnan effect [46]. However, the positive field on the membrane surface could be greatly affected by divalent counter-ion SO_4^{2-} . The lower MgSO_4 rejection compared to MgCl_2 could be due to the weakened Donnan effect. Nevertheless, the rejection of MgSO_4 was still >90%, higher than many PEI-based polyamide membranes with a positively charged surface, which could be due to the tighter polyamide network as the result of the addition of PIP in this study.

Figure 11: Zeta potential of the ceramic substrates and the polyamide thin film composite membranes PA-100 and PA-200

3.4 Performance of polyamide-ceramic membranes under high temperatures

As ceramic substrates have high chemical and thermal stabilities, polyamide-ceramic composite membranes could be potentially useful for more challenging applications such as organic solvent or high temperature nanofiltration. In this study, we tested the nanofiltration performance of the resultant membranes at high temperature up to 80 °C and the results are shown in Figure 12 (a). During the experiment, the membrane PA-100 was first tested at room temperature and the temperature of the feed solution was then increased to 50, 60, 70 and 80 °C, before it was decreased back to room temperature. The rejections of all these 4 solutes decreased with the increase in temperature, which could be caused by the enlarged effective “pore size” of polyamide at high temperature [47]. The rejection of PEG-300 dropped below 90 % at high temperature, 50 °C and above. However, the membrane still showed excellent sucrose rejection >95% even at 80 °C, showing a great potential of the membranes in high temperature food processes. The rejection rates of all solutes were recovered when the temperature was reduced back to room temperature, indicating that the polyamide layer was still in good condition after experiencing high temperature. The membrane also showed good MgCl_2 rejection at high temperature, though the rejection of MgSO_4 dropped below 90% when the temperature was higher than 50 °C. The decrease in MgSO_4 rejection could be caused by the enlarged pore size while the effect of surface charge on rejection of MgCl_2 was not affected significantly by the elevated temperature. Furthermore, the rejection of MgCl_2 at 70°C was run for 48 hours and the membranes exhibited good stability, as shown in Figure 12 (b). Ceramic substrates have a high thermal stability compared to most polymeric substrates. The swelling of polymeric substrate at high temperature may damage the thin polyamide layer and many commercial polyamide membranes could not be used above 50 °C. With the MWCO remaining small (~340 Da) and the increase in permeation flux at high temperature, polyamide-ceramic composite membrane could be useful for nanofiltration where the feeds are at elevated temperature.

Figure 12: Performance of the membrane PA-100 in high temperature nanofiltration (a) Rejection of MgCl₂, MgSO₄, sucrose and PEG-300 at varied temperature. The temperature was increased from 25 to 80 °C, and then back to 25 °C. (b) Rejection of 1000 ppm MgCl₂ at 70 °C. The membrane showed good thermal stability with a consistent performance throughout 48 hours.

We also compared the polyamide-ceramic composite membranes synthesized in this study with other ceramic composite membranes reported recently, as listed in Table 2. Only hollow fibres, tubular membranes and monoliths are compared, as ceramic membranes of these geometries have a higher potential to scale up. Four major techniques have been applied in recent studies to synthesize nanofiltration ceramic membranes. Almost all the membranes showed high PWP $>15 \text{ LMH bar}^{-1}$, though most of their MWCO was larger than 500 Da. The sol-gel method demonstrated the possibility to produce nanofiltration membranes from microfiltration substrates. However, it required multiple steps and a high temperature treatment. The atomic layer deposition was used to fine tune the pores of nanofiltration membranes but it may not be feasible for substrates with large pore sizes. The layer-by-layer was a simple technique to synthesize nanofiltration membranes though the chemical resistance of the coating layer may not be as strong as the polyamide membranes. The polyamide-ceramic composite membranes synthesized in this study had a relatively small MWCO while maintaining a high PWP. The membranes also showed high rejection of divalent ion salts, for both MgCl_2 and MgSO_4 . Therefore, the membranes exhibited a great potential for various applications, from water treatment to nutrient recovery [48], especially for challenging process feeds.

Table 2: Nanofiltration ceramic and ceramic composite hollow fibres, tubular membranes and monolith synthesized using various techniques in recent years

Technique	Selective layer	Substrate		PWP (LMH bar ⁻¹)	MWCO (Da)	Salt rejection (%)		Salt concentration (ppm)	Operating pressure (bar)	Ref., Year of publication
		Type	Pore size (nm)			MgCl ₂	MgSO ₄			
Sol-gel	γ-Al ₂ O ₃	HF	229	17.4	1400	~85 ^a	~7 ^a	2000	5	[49], 2016
	γ-Al ₂ O ₃	Tube	200	24.8	1000	~92 ^a	~6 ^a	0.005 mol/L	4	[50], 2015
ALD	TiO ₂	Tube	5	30	680	-	-	-	-	[51], 2017
	TiO ₂	Tube	0.7	11-16	260-380	-	-	-	-	[52], 2017
LBL	PDADM AC/ PSS	ML	100	15	240	-	83.8	601	3.5	[53], 2016
	PSS/ZIF8	Tube	100	21	500-600	-	-	-	-	[54], 2015
IP-PA	PEI/TMC	HF	100 ^b	26.4	430	95.5	84	2000	4	[29], 2018
	PIP/TMC	HF	280 ^b	2-5	974 ^c	-	-	-	-	[27], 2018
	PEI/PIP/ TMC	Tube	100	16.7	240	94.1	91.5	2000	4	This work
			200	18.4	260	93.8	90.1	1000	2	

Note:

^a. The data was read from the figures

^b. An intermediate layer was coated to reduce the pore size

^c. Only the rejection of rose bagel was tested in the study

Abbreviations: ALD atomic layer deposition, LBL layer by layer, IP interfacial polymerization, PA polyamide, PDADM polydiallyldimethylammonium chloride, PSS poly(sodium 4-styrene sulfonate)

4. Conclusions

Polyamide thin films were successfully synthesized on microfiltration ceramic tubular membrane substrates via interfacial polymerization. The solvent washing step created a stable aqueous-organic interface on the substrate surface, enabling the formation of continuous polyamide thin film on the substrate. The thin film showed a good integration with the ceramic substrates. The mechanical property of the polyamide thin film was examined carefully and the modulus was successfully measured using the AFM pinpoint mode. The composite membranes showed excellent performance in nanofiltration with a PWP of 16-18 LMH bar⁻¹ and a MWCO of about 250 Da. The high PWP could be attributed to the loose PEI-based polyamide network and the porous ceramic substrate. The membranes also exhibited good rejections of organic dyes and divalent salts such as CaCl₂, MgCl₂ and MgSO₄, showing great potential for water treatment. When tested at high temperature, the membranes still showed high rejection to sucrose and MgCl₂. As the ceramic substrates used were highly inert, the membranes could be potentially applied in applications involving organic solvent, high temperature as well as at a wide pH range. This study also demonstrated a simple approach to fabricate nanofiltration composite membranes from commercial ceramic microfiltration membranes.

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