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**Polyamide-imide hollow fiber membranes crosslinked with amine-appended
inorganic networks for application in solvent-resistant nanofiltration
under low operating pressure**

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Abstract

The development of polyamide-imide (PAI) hollow fiber membranes for solvent-resistant nanofiltration (SRNF) in polar aprotic solvents such as dimethylformamide (DMF) under low operating pressure of 2 bar is reported in current study. Highly porous PAI substrates were fabricated and crosslinked with (3-aminopropyl)trimethoxysilane (APTMS). The resultant membranes were solvent-stable and showed higher hydrophilicity and better mechanical property. A 30-minute conditioning with either isopropanol or deionized water after the crosslinking reaction was found to affect the morphology of the membranes and thus their nanofiltration performance. Membranes conditioned with isopropanol consistently showed higher solvent fluxes coupled with lower rejections of Rose Bengal (RB) ranging 75-87%. On the other hand, membranes conditioned with deionized water had lower fluxes and high RB rejections of 96-99%. The best-performing membrane achieved a permeability of 6.4 L/(m².h.bar) in IPA and 0.9 L/(m².h.bar) in DMF with RB rejections of over 97% and 98%, respectively, under 2 bar operating pressure, showing their potential to be used in SRNF processes effectively.”

Keywords: Polyamide-imide; Hollow fiber membrane; Organic-inorganic network; Solvent-resistant nanofiltration.

1. Introduction

The development of membranes for solvent-resistant nanofiltration (SRNF) processes have expanded their application potential in various industries such as petrochemical, food, fine chemical and pharmaceutical industries. By separating molecules ranging in 200-1000 Da through applying a pressure gradient across a membrane, SRNF can offer many advantages over conventional industrial separation processes, such as lower energy consumption and recycling of valuable solvents and reagents [1]. The key challenges faced in developing SRNF membranes lie in ensuring their excellent stability in organic solvents and achieving acceptable solvent permeabilities and target solute rejections over long-term operation. The majority of SRNF membranes that have been developed in the lab or commercialized are made from polymeric materials due to their lower cost, excellent processability and ease of scale-up. Significant progress has been made over the past decade to improve the stability of polymeric membranes especially in aggressive solvents like dimethylformamide (DMF) and N-methyl pyrrolidone (NMP), for which integrally skinned asymmetric (ISA) and thin film composite (TFC) membranes have been developed [2-6].

TFC membranes usually comprise of polydimethylsiloxane (PDMS) [7, 8] or polyamide [5, 9, 10] on a porous support while the polymers that have been used to fabricate integrally skinned asymmetric SRNF membranes include polyimide (PI) [2, 3, 11-13], polysulfone [13-15], polyphenylsulfone (PPSU) [16-18], poly(ether ether ketone) (PEEK) [19-22], polyaniline [4, 23, 24] and polybenzimidazole [25, 26]. The crosslinking of polymer chains to form stable three-dimensional network structures has been shown to improve the chemical and mechanical stability of membranes. In particular, crosslinked polyimide membranes have found their application in SRNF in addition to gas separation and pervaporation [27]. For example, Lenzing P84[®] polyimide membranes showed good

chemical stability in NMP, DMF, tetrahydrofuran and dichloromethane after being crosslinked by aliphatic diamines [2]. Recently, Siddique et al. [28] reported the advantages of using 3-aminopropyl trimethoxysilane (APTMS) as the crosslinking agent. Through the hydrolysis and condensation of methoxysilane in APTMS, a rigid inorganic Si-O-Si network was obtained throughout the polyimide membrane, thus improving the mechanical properties of the membrane in addition to its chemical stability. Dutczak et al. [29] successfully crosslinked commercial polyamide-imide (PAI) support membranes using diisocyanates. The crosslinked membranes were resistant to NMP and showed good mechanical properties.

Currently, commercial SRNF membranes are limited to a few flat sheet and spiral-wound modules [30]. Hollow fiber SRNF membranes are not known to be commercially available although they have the potential to make the process more efficient and attractive by operating at lower pressures and providing a higher membrane area to module volume ratio which enables the construction of more compact and simpler modules that are easy to scale-up [31]. The few hollow fiber membranes that have been applied in SRNF so far were evaluated at around 5 bar [18, 24]. Literature has reported nanofiltration hollow fibers for water softening applications that are capable of operating at pressures as low as 2 bar, which would help to reduce energy consumption, increase productivity and lower costs [32-34]. Low pressure operation was possible due to the fabrication of a highly porous substrate that could reduce mass transfer resistance significantly, thus allowing the resultant composite membrane to achieve high flux and rejection. A similar strategy will be attempted in this study to develop hollow fibers that can be applied in SRNF under low pressure.

This study aims to fabricate and crosslink polyamide-imide (PAI) hollow fiber membranes to make them suitable for SRNF applications. PAI is chosen due to its excellent processability, mechanical property and good chemical and thermal stability [35]. PAI hollow fibers can be fabricated easily by non-solvent induced phase separation technique and have shown good performance in forward osmosis process after modification on a porous ultrafiltration substrate [36, 37]. After fabrication, the PAI membranes will be crosslinked with APTMS through a ring-opening reaction between the imide groups of PAI and amine groups of APTMS which was previously confirmed by Zhang et al. [38]. To the best of our knowledge, this is the first study to develop PAI hollow fiber membranes for application in polar aprotic solvents under low operating pressure of 2 bar. The morphology, gel content, swelling, contact angle and mechanical strength of the modified membranes will be characterized and their performance in two common solvents, isopropanol (IPA) and DMF, will be evaluated.

2. Experimental

2.1. Materials

Polyamide-imide (PAI) Torlon[®] 4000T-MV, supplied by Solvay Advanced Polymers, was used to fabricate hollow fiber substrates. N-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck) and lithium chloride (LiCl, anhydrous, CAS#7447-41-8, MP Biomed) were used as the solvent and additive for preparing the dope solution respectively. Dextran with molecular weights from 6-500 kDa (CAS#9004-54-0, Sigma) were used to characterize the molecular weight cut-off (MWCO) of the hollow fiber substrates. The substrates were crosslinked with (3-aminopropyl)trimethoxysilane (APTMS, 97%, CAS#13822-56-5, Sigma). Raffinose (594.52 Da, CAS#17629-30-0, Merck), polyethylene glycol (PEG, 1 kDa, CAS#25322-68-3, Merck, and 2 kDa, Sigma) were used to measure the

pore size distribution of the crosslinked membranes. For nanofiltration tests, iso-propanol (IPA, $\geq 99.8\%$, CAS#67-63-0, Merck) and N,N-dimethylformamide (DMF, CAS# 68-12-2, Merck) were used as the solvents and Rose Bengal (1017.64 Da, 95%, CAS#632-69-9, Sigma) was employed as the model solute. Milli-Q deionized water (18M $\Omega\cdot\text{cm}$) was used in all aqueous solutions. All the reagents were used as received. The chemical structures of PAI and APTMS are given in Fig. 1.

2.2. Fabrication of PAI hollow fiber substrates

Torlon[®] 4000T-MV was dried in a vacuum oven at 50 °C for at least 12 hours to remove moisture before preparing the dope solutions. The polymer and LiCl were dissolved in NMP in a jacket flask and mechanically stirred for 3-4 days at 60 °C until a homogenous dope solution was obtained. Then, the solution was cooled to room temperature and degassed under vacuum overnight before spinning. A dry-jet wet spinning technique was used to fabricate the hollow fiber substrates. The dope and bore fluid were extruded through a spinneret at controlled flow rates and went through an air gap before entering the coagulation bath. The hollow fibers were collected by a roller and stored in tap water for 2 days to remove residual solvent. Subsequently, they were stored in deionized water for further use. Three batches of substrates, designated #1, #2 and #3, were fabricated under different spinning conditions as summarized in Table 1.

2.3. Post-treatment of PAI hollow fiber substrates

The hollow fibers were immersed in a 2% (wt/vol) APTMS solution in a 1:1 volume mixture of IPA and deionized (DI) water at 60-80 °C for 1-5 hours. The membranes were then subjected to conditioning treatment for 30 minutes in either IPA or DI water to remove the excess crosslinker and subsequently dried overnight in ambient air.

2.4. Characterization of membranes

The cross-section, inner and outer surface of the hollow fiber membranes were observed using the Field Emission Scanning Electron Microscope (FESEM) JEOL JSM-7600F at an operating voltage of 5.0 kV. Prior to analysis, the membrane samples were broken in liquid nitrogen and then sputtered with a thin layer of platinum at 20 mA for 30 seconds using JEOL JFC-1600 Auto Fine Coater. The FESEM was equipped with an energy dispersive X-ray spectrometer (EDX) for elemental mapping analysis. The functional groups on the surface of the membranes were analysed by a Fourier transform infrared spectrometer (FTIR, IRPrestige-21, Shimadzu) via attenuated total reflection (ATR) method.

The dynamic contact angle of the hollow fibers was measured by a tensiometer (DCAT11 Dataphysics) to determine the hydrophilicity of the membranes. For each measurement, a short fiber sample was fixed by the sample holder and experienced 5 consecutive cycles of immersion into and emersion from DI water. Based on the interaction forces, geometry of the membrane and known surface tension of the water, the advancing and receding contact angles of the membranes were calculated by the equipment software using the Wihelmy method. The stress-strain behaviour of the membranes was evaluated by tensile tests using a Zwick Roell Z0.5 universal testing machine at room temperature. The hollow fiber sample was clamped at both ends and pulled in tension at constant elongation velocity of 50 mm/min with an initial grip to grip separation of 25 mm. Tensile modulus, tensile stress and tensile strain at break were automatically calculated by the software.

The overall membrane porosity, ε_m , is defined as the volume of the pores over the total membrane volume and calculated by equation (1):

$$\varepsilon_m = \frac{(m_1 - m_2) / D_I}{\frac{m_1 - m_2}{D_I} + \frac{m_2}{D_P}} \quad (1)$$

where m_1 is the weight of wet membrane after soaking in IPA, m_2 is the dry weight of membrane, D_I is the density of IPA, and D_P is the density of polymer, which was taken to be 1.42 g/cm³ for PAI.

To measure the pure water permeability (PWP) of the substrates, 4 membrane fibers were assembled in a tube and deionized water was circulated through the shell side of the hollow fibers at 1 bar for 1 hour to allow for membrane compaction and water flux to stabilize. The PWP was calculated according to the equation:

$$J = \frac{Q}{A_m \times \Delta P} = \frac{Q}{n\pi D L_{eff} \Delta P} \quad (2)$$

where J is the pure water permeability (L/(m².h.bar)); Q is flow rate of permeate (L/h); A_m is membrane area (m²); ΔP is the system pressure (bar); n is the number of fibers in the module; D is the outer diameter of the hollow fiber (m) and L_{eff} is the effective length of the module (m). To measure the MWCO of the substrates, a 2000 ppm aqueous solution containing dextran with molecular weights ranging from 6000 to 500,000 Da was filtrated from the shell side and lumen side of the hollow fibers respectively at 1 bar. A feed sample was collected at the start of filtration and permeate was collected after 30 minutes. Analysis of the dextran was performed by gel permeation chromatography (GPC) using a Polymer Laboratories-GPC 50 plus system. The MWCO was defined as the molecular weight of dextran that was retained by 90%.

To measure the pore size distribution of the crosslinked membranes, 200 ppm aqueous solutions of raffinose and PEG (1 and 2 kDa) were filtrated from the shell side of

the hollow fibers at 1 bar. The concentration of each solute in the feed and permeate were analyzed using a Total Organic Carbon analyzer (TOC_VCSH, Shimadzu) and the pore size distribution was obtained by using a two-parameter log-normal distribution function described elsewhere [39, 40].

The gel content defined as the amount of material that remains undissolved in a certain solvent was measured to quantify the stability of modified membranes in DMF [11]:

$$\text{Gel content (\%)} = \frac{W_f}{W_i} \times 100 \quad (3)$$

where W_f is the final dry weight of crosslinked membrane after 2-week immersion in DMF and W_i is the initial dry weight of crosslinked membrane. Fibers of 10 cm in length were immersed in IPA or DMF and their initial and final lengths were measured. The percentage change in length of the fibers was calculated to evaluate their swelling behavior [41].

2.5. Nanofiltration tests

The performance of the crosslinked membranes was measured by the solvent flux and rejection of the dye, Rose Bengal (RB), in IPA and DMF, respectively. The solute concentration was fixed to 35 μM which is commonly used for lab-scale SRNF experiments [11]. Cross-flow filtration of pure solvents was first performed from the shell side of the hollow fibers at 2 bar and room temperature to determine the pure solvent permeability after solvent fluxes were stabilized. Next, the membranes were filtrated with 35 μM RB solution under the same conditions. After 1 hour, permeate was collected and weighed to calculate the solvent flux and permeability while the concentration of RB in the feed (C_f) and permeate (C_p) were measured by Shimadzu UV-1800 UV spectrophotometer at wavelength

of 558 nm. Rejection of RB was calculated using equation (4). All measurements were carried out with at least three samples and the average values were reported.

$$\text{Rejection (\%)} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

3. Results and Discussion

3.1. Characterization of PAI hollow fiber substrates

The properties of the hollow fiber substrates are summarized in Table 2. They have similar wall thickness and PWP, but differ in their outer and inner skin MWCO values. The analysis on MWCOs of membranes revealed that #2 and #3 have a denser outer skin than that for #1. The inner and outer skins of #1 seem to be equally dense, while #3 showed the highest difference in MWCOs of inner and outer skins. Comparing #1 and #2, the higher bore fluid flow rate resulted in faster diffusion of bore fluid through the membrane such that the polymer concentration at the outer surface was reduced at a faster rate. This could explain why #2 has a lower outer skin MWCO than #1.

The cross-section and outer surface morphologies of the substrates are shown in Fig. 2. All of them have finger-like structures developed from the inner and outer surfaces of the membranes with a thin sponge-like structure in the middle. The outer surfaces of the membranes are observed to be smooth with no large pores or defects. The substrates prepared in this work possess a uniform structure with a narrow pore size distribution which could facilitate more uniform crosslinking of the membranes.

3.2. Optimization of crosslinking conditions

To improve the stability in aggressive solvents, the hollow fiber substrates were crosslinked with APTMS that could form inorganic network structures inside of the substrates. An excess amount of APTMS was introduced with a concentration fixed at 2%. To determine the optimal crosslinking temperature and time, substrate #1 was treated with APTMS at varying temperatures of 60 to 80 °C for 1 hour and conditioned with DI water. The mechanical properties of the resultant membranes are shown in Table 3. The rigidity of the membranes increased as indicated in the increase in tensile modulus. However, the crosslinking at high temperature such as 80 °C made the membranes too brittle to be used in nanofiltration processes. Thus, subsequent modification was chosen to be carried out at 60 °C.

The effects on gel content, contact angle and mechanical properties of #1 membranes crosslinked at 60 °C for 1 to 5 hours are summarized in Table 4. Gel content of the original substrate could not be measured due to its dissolution in DMF. A high gel content of over 90% was obtained for all membranes owing to the formation of crosslinking of polymer chains with the amine-tethered inorganic networks which will be verified in section 3.3.1. With increasing reaction time, the gel content increased to over 98% for crosslinking time of 3 hours and beyond. The contact angle of the membranes decreased with increasing treatment time, indicating that membranes became more hydrophilic. This could be due to the presence of more silanol (Si-OH) groups on the membrane surface as more APTMS reacted with the polymer. As the membranes crosslinked for 5 hours became too brittle and there was no significant increase in gel content, the optimal reaction time was chosen to be 3 hours.

In subsequent experiments, the three substrates were crosslinked with 2% APTMS at 60 °C for 3 hours. For each substrate, one batch of membranes was conditioned with IPA

(denoted as #x-I, x is the substrate number) while another batch was conditioned with DI water (denoted as #x-H) after immersing in the APTMS solution. The gel contents of all the crosslinked membranes were similar regardless of the **conditioning** solution, while marginal differences were observed in the contact angle and mechanical properties of #x-I membranes compared to that of #x-H membranes. Hence, it appears that the different **conditioning** solutions did not affect the gel content, hydrophilicity or mechanical properties of the membranes significantly.

3.3. Characterization of crosslinked hollow fiber membranes

3.3.1. FTIR and elemental mapping analysis

The FTIR spectrum of #1 membranes before and after crosslinking with 2% APTMS at 60 °C for 3 hours is shown in Fig. 3. The spectra of #1-H and #1-I membranes were similar. Characteristic imide peaks were observed for the original substrate at 1778, 1691 and 1375 cm^{-1} . After crosslinking, the imide peaks disappeared while the intensity of amide peaks at 1641 and 1535 cm^{-1} became stronger. These peaks agree with a previous report [38] and confirm that the PAI substrate was successfully crosslinked by APTMS. A stronger peak observed at 1089 cm^{-1} could be attributed to the Si-O-Si bond [42] which forms the inorganic network within the membrane.

EDX was used to analyze the cross-section of the crosslinked membranes and a representative map showing the distribution of Si for #1-H membrane is shown in Fig. 4. A uniform distribution of silica throughout the entire membrane cross-section can be observed and this indicates that the silica inorganic network was successfully formed in the whole membrane.

3.3.2. Membrane morphology

The cross-section and outer surface morphologies of #2 membranes are shown in Fig. 5. In Fig. 5a, finger-like structures can still be seen in the crosslinked membranes but their sizes are reduced. It is likely that crosslinking decreased the porosity of the membranes by closing or blocking some of the membrane pores. As shown in Fig. 5b, the outer skin layer was observed to be thicker in the crosslinked membranes with an estimated average thickness of 1.5 μm compared to that of pristine membrane (0.7 μm). From visual observation of Fig. 5c, the outer surfaces of the crosslinked membranes appeared rougher than those for pristine membrane as small spherical particles were observed to be embedded in the membranes as well as on the surface, where their density is generally higher in #x-H membranes compared to #x-I ones. These particles are most likely silica particles formed by the condensation of APTMS. A possible reason for the higher number of silica particles found in #x-H membranes could be the condensation residual APTMS facilitated by the DI water. Meanwhile, conditioning with IPA might allow the unreacted APTMS to be removed from the membrane easier and faster.

3.3.3. Swelling of hollow fibers

To investigate the swelling properties of membranes, the length of each hollow fiber sample was measured before and after the immersion in solvents. The untreated substrates showed a 5% increase in length after immersion in IPA for 5 hours and no more change was observed after that. In contrast, the crosslinked hollow fibers showed improved swelling resistance such that the length of fibers increased only 1-2% after immersion in IPA. However, increased swelling was observed when the crosslinked fibers were immersed in DMF as they experienced a 4-5% increase in length. Overall results indicate that some swelling effects were still present in crosslinked membranes although the degree of swelling

was reduced compared to that of untreated hollow fiber. Note that the swelling property of the PAI membranes in this work is comparable with that of PPSU hollow fibers fabricated by Darvishmanesh et al. [18].

3.4. Nanofiltration performance

The solvent filtration performance of the membranes was conducted under a relatively low pressure of 2 bar. The highly porous hollow fiber substrate with a very thin wall made it possible (see Table 2) by reducing mass transfer resistance. The solvent filtration performance of the membranes are presented in Figs. 6 and 7. All membranes prepared in this work showed higher solvent flux for IPA than that for DMF as observed in previous work [43-46]. Although the different conditioning solutions caused minor changes in the membrane properties such as their gel content, contact angle, mechanical properties and degree of swelling, a significant difference was observed in the solvent fluxes and RB rejections between #x-I and #x-H membranes. #x-I membranes consistently showed higher solvent fluxes and thus higher solvent permeabilities coupled with lower RB rejections ranging 75-87%. On the other hand, #x-H membranes had lower permeabilities and high RB rejections of 96-99%.

This difference is most likely caused by the changes in membrane morphology as described in Section 3.3.2. The high density of silica particles in membrane may be a major reason why #x-H membranes had lower fluxes than #x-I membranes as they may lead to pore blockage. This can explain the difference in pore size distribution of the membranes as shown in Fig. 8. The membranes conditioned with H₂O had lower mean pore diameters and narrower pore size distributions, which can explain their lower permeability and higher rejection values compared to membranes conditioned with IPA. Out of the membranes

conditioned with H₂O, #1-H had a larger mean pore size and slightly broader pore size distribution than #2-H and #3-H, which could be attributed to #1 substrate having the least dense skin layer. Thus it showed the largest solvent flux while rejection was not compromised. This is likely because its pore size and relatively narrow pore size distribution remained tight enough to reject RB molecules. #2-H and #3-H, having substrates with similarly dense skin layer, had similar pore size distribution and mean pore size. However, as #3 had a more porous inner skin which suggests less mass transfer resistance, the solvent flux of #3-H was higher than that of #2-H although rejections were similar. #2-H became so dense such that the IPA flux was very low and no DMF flux could be obtained. On the other hand, when membranes were conditioned with IPA, less silica particles were found on the membrane surface, reducing the extent of pore blockage. As a result, the membranes showed higher mean pore diameters and broader pore size distributions, which led to higher solvent fluxes but lower rejections.

#1-H membrane was chosen to be subjected to extended filtration tests to investigate their long-term stability and the results are presented in Fig. 9. Over the 7-day testing period in IPA, the membranes showed a slight decrease in flux and showed IPA permeability of 6.4 L/(m².h.bar) with RB rejections above 97%. Testing of the membranes in DMF was limited to a 3-day period due to the instability of the epoxy used to seal the module. DMF permeability was relatively stable at 0.9 L/(m².h.bar) while rejections of over 98% were achieved.

The performances of various integrally skinned asymmetric SRNF membranes that were tested in RB solutions are listed in Table 5. #1-H membrane showed a much higher IPA permeability compared to the PPSU hollow fiber reported previously, although the RB

rejection decreased slightly. The DMF permeability of the membrane also falls within the typical range, and it should be noted that the PAI HF membranes in this work were tested at a relatively low pressure of 2 bar compared to that in previous studies. Our future effort will be devoted to improve the solvent permeability further.

4. Conclusions

PAI hollow fiber substrates were fabricated by non-solvent induced phase inversion method and crosslinked by forming amine-tethered inorganic networks in the membrane to improve their stability in aggressive solvents like DMF. The optimization of crosslinking conditions led to a good stability of the membrane in organic solvents together with improved mechanical property and hydrophilicity.

The different **conditioning** method after the crosslinking reaction affected the morphology and thus the nanofiltration performance of the membranes. Higher solvent permeabilities and moderate RB rejections of 75-87% were observed for membranes conditioned with IPA after crosslinking, while lower permeabilities and high rejections of 96-99% were obtained from membranes conditioned with DI water. The best-performing membrane achieved a permeability of 6.4 L/(m².h.bar) in IPA and 0.9 L/(m².h.bar) in DMF with rejections over 97% and 98% respectively. These hollow fiber membranes were able to be tested at a lower operating pressure of 2 bar than that in previous studies and with further development, they show potential to be used in SRNF processes and make them more efficient and economically viable.

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