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Identification of safe and stable operation conditions for pressure retarded osmosis with high performance hollow fiber membrane

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Abstract

Pressure retarded osmosis (PRO) is a promising energy harvesting technique. However, when polymeric hollow fiber membrane is used for the PRO process, the mechanical strength of the membrane is a big concern. As hollow fiber membrane is self-supported and due to its polymeric nature, it may gradually deform over time under high pressure loading, or membrane “creeping” will occur. **Current work is the first attempt to analyze the membrane creeping phenomenon of a novel thin film composite (TFC) hollow fiber.** The membrane creeping was evaluated via nanoindentation by using atomic force microscope (AFM). A non-stop 200-hour PRO test and integrity check, which have not been reported previously, were carried out to investigate the membrane performance under various operating pressures. The results show that the membrane is able to produce a stable power density output of 19.2 W/m² at 15.0 bar, using 1.0 M NaCl as the draw solution and DI water as the feed water. Membrane creeping was observed when the applied pressure exceeded the safe operation **limit (or the flux turning point, where the membrane flux started to increase with increasing applied pressure in the PRO mode), which caused an irreversible damage to the membranes.** This study identified safe and optimum operation conditions of the laboratory-made PRO hollow fiber membrane to achieve the most favourable PRO performance. It provides guidance for practical applications of polymeric hollow fiber membranes in PRO process.

Keywords: *pressure retarded osmosis, hollow fiber membrane, Membrane creeping, stability test, optimum working pressure*

Highlights:

- Deformation of PRO hollow fiber membrane was found under high pressure loading
- Membrane creeping was evaluated via nanoindentation by using AFM
- PRO water flux turning point is an indicator for creeping commencement.
- Optimum working pressure of PRO hollow fiber membrane was identified.

1. Introduction

Over the last century, global population grew considerably and the global economy developed rapidly. As a result, the demands for water and energy have been intensified world-wide, which stimulated the exploitation of new energy resources. Osmotic energy, where pressure retarded osmosis (PRO) system could potentially be used to harvest a significant amount of renewable energy from two streams with different salinities, was first proposed by Loeb in 1970s [1]. However, due to limited availability of commercial membranes on the market, few PRO experiments were conducted to improve the technology [2, 3]. Recently, the PRO technology gains increasing popularity with advancement in membrane fabrication technology, which potentially offers a renewable solution for the depletion of the world's petroleum reserves.

Based on the osmotic process type, membranes can be classified as reverse osmosis (RO), forward osmosis (FO) or direct osmosis (DO) and pressure retarded osmosis (PRO). RO utilizes hydraulic pressure to overcome the osmotic pressure difference to push freshwater from a high salinity solution to a low salinity solution across a semi-permeable membrane. RO has been extensively studied and utilized for seawater desalination and waste water reclamation [4-6]. FO, on the other hand, is a concentration-driven process where water diffuses naturally from a low salinity solution to a high salinity solution across a semi-permeable membrane. In spite of its inability to produce freshwater directly, FO has attracted much attention recently for several potential applications and hybrid systems [7-10]. PRO is an osmotic energy-recovering process that derives from the natural phenomenon of osmosis. Similar to FO process, water transfers from a low salinity solution at ambient pressure via a

selectively permeable membrane to a pressurized high salinity solution. The increased volume of pressurized solution is able to drive a turbine for power generation [11].

Though PRO has been intensively studied recently, many problems need to be addressed. Studies on PRO processes reveal that experimental PRO water flux tends to be significantly lower than the theoretical values due to internal concentration polarization (ICP). The presence of ICP reduces the effective osmotic driving force resulting in a lower power density [12]. ICP was first discussed in late 1970s [2], and further developed into a conceptual model by the early 1980s. According to the model developed by Lee *et al.* [3], it is possible to eliminate ICP if the mass transfer resistance is minimized. Subsequently, the ideal support layer for PRO is thought to be as thin and porous as possible [13]. On the other hand, the membrane should possess an excellent mechanical strength to withstand high hydraulic pressures and long term operation. Theoretically, a maximum power density exists when the hydrostatic pressure difference is equal to half of the osmotic pressure difference, suggesting the optimal working condition for a PRO system.

Many attempts have been made to fabricate high performance osmotic-driven membranes both in hollow fiber and flat sheet configurations. Generally, an FO/PRO membrane consists of an RO-like selective layer supported by a permeable layer providing the necessary mechanical support with the least mass transfer resistance. A commercial flat sheet osmotic membrane made of cellulose triacetate (CTA, HTI) embedded on a polyester woven mesh has been used in a PRO process. The membrane is able to withstand a hydraulic pressure of 17 bar and power density of 5.8 W/m^2 can be achieved [14]. A polybenzimidazole (PBI) – polyacrylonitrile (PAN) dual-layer thermally annealed hollow fiber membrane had a peak power density of 5.1 W/m^2 at 15 bar when 1.0 M NaCl and 10 mM NaCl were used as the

draw and feed solutions, respectively [15]. Hollow fiber membranes made from polyethersulfone (PES) as the support layer and a thin film composite (TFC) of polyamide as the selective layer was fabricated for FO applications. It was found that the finger-like structure of pores in the support layer is able to greatly mitigate the ICP effect [16]. This method was further improved to fabricate a PRO membrane with a power density of 11 W/m^2 at 9 bar [12]. Moreover, to further enhance the mechanical strength, polyetherimide (PEI) was used as the substrate material and the structure of the hollow fiber membrane was controlled to give a sponge-like morphology. This membrane was able to achieve power density of 20.9 W/m^2 at 15.1 bar operating pressure [17]. Zhang *et al.* developed thin film composite PES hollow fiber membranes with power density of 24.3 W/m^2 at 20 bar by using 1.0 M NaCl as the concentrated brine and DI-water as the feed water [18].

However, it should be pointed out that while different types of PRO membranes have been developed, the long-term PRO performance of resultant membranes and comprehensive integrity check were not reported in the literature. Investigations on membrane stability tested over long-term operation have been elusive. It is well understood that due to its polymeric nature, polymeric membrane may gradually deform over time under high pressure loading, or membrane “creeping” will occur. The creeping phenomenon would eventually damage the membrane and deteriorate the membrane performance to complete failure.

The current study aims to investigate the stability of an in-house made high performance PRO hollow fiber membrane in order to identify safe and stable operating conditions over long term testing under a high hydraulic pressure. The support layer was made of PEI, providing an excellent mechanical support and low trans-membrane mass-transfer resistance. The selective layer of polyamide was prepared by interfacial polymerization. The PRO

hollow fiber membrane was pressurized at various hydraulic pressures in RO and PRO modes in order to understand its performance behaviour. After obtaining an entire picture, the membrane was pressurized at specific hydraulic pressures for a long period of time to study the time effect. The PRO hollow fiber membranes were then characterized using various techniques including nanoindentation by using AFM for membrane creeping evaluation. The performance of the PRO hollow fiber membranes was tested on a laboratory scale PRO setup. This study is believed to be the first effort to investigate the creeping phenomenon of PRO hollow fiber membrane due to high pressure loading and to report PRO membrane performance over a long term test of 200 hours. It is expected to provide guidance for practical applications of polymeric hollow fiber membranes in PRO process.

2. Experimental methods

2.1. Materials

Polyetherimide (PEI Ultem 1000, GE Plastic, USA) was used to make the porous hollow fiber substrates. N-methyl-2-pyrrolidone (NMP, > 99.5%, CAS#872-50-4, Merck Chemicals, Singapore) was used as the solvent. Polyethylene glycol (PEG, CAS#25322-68-3, Merck Chemicals, Singapore) was used as a pore former for the substrate. Purified water by a Milli-Q system (18 MΩ cm) and tap water were used as the bore fluid and the external coagulant, respectively. Dextrans with different molecular weights (6,000-500,000 Da; (C₆H₁₀O₅)_n, Sigma Aldrich) were used to determine the molecular weight cut off (MWCO) of the substrate. Glycerol (85%, CAS#56-81-5, Merck Chemicals, Singapore) was used to post-treat the membrane for storage purposes. 1,3,5-Benzenetricarbonyl trichloride (TMC, CAS# 4422-95-1, Sigma-Aldrich) and *m*-phenylenediamine (MPD, CAS# 108-45-2, Sigma-Aldrich) were

used as the monomers for the interfacial polymerization. Cyclohexane (CAS# 110-82-7, Merck Chemicals, Singapore) was used as the solvent for TMC. Sodium chloride (NaCl, CAS# 7647-14-5, Merck Chemicals, Singapore) was used to prepare the feed and draw solutions.

2.2. Fabrication of PRO hollow fiber membranes and modules

PEI hollow fiber substrates were fabricated based on the non-solvent induced phase separation (NIPS) method by a dry jet-wet spinning technique. The polymer and the additive were completely dissolved in NMP prior to spinning. The details of the hollow fiber spinning process and post-treatment can be found elsewhere [17, 19].

Fifteen pieces of hollow fibers were potted into a tube with effective length of 22 cm and sealed by epoxy. The active-selective layer was subsequently developed on the inner surface of the PEI hollow fiber substrates by interfacial polymerization of TMC and MPD at ambient temperature as described in the literature [9]. The hollow fiber membranes with the selective layer would be known as PRO-PEI HF.

2.3. Characterizations and analysis

The dimension of PEI hollow fiber substrates was measured by a Keyence VHX 500F Digital Microscope. A mean value was obtained based on the measurement of ten different fibers. The structure and morphology of the fiber cross-section and surface were examined by a Jeol JSM-7600F field emission scanning electron microscope (FE-SEM). The wet hollow fiber

membranes were dried in a freeze drier overnight prior to be fractured in liquid nitrogen. The samples were subsequently mounted on the SEM stubs followed by platinum sputter coating.

Pure water permeability (PWP) and molecular weight cut off (MWCO) of PEI hollow fiber substrates were tested by using a bench scale cross-flow filtration system at a constant pressure of 1 bar. Ten pieces of hollow fiber substrates were potted into a tube (with effective length of 25 cm) and sealed by epoxy. Distilled water was circulated through the lumen side of the module to get PWP. The MWCO of PEI hollow fiber substrate was determined by the filtration method using a 2000 ppm dextran solution and analyzed by gel permeation chromatography (GPC) on a Polymer Laboratories-GPC 50 plus system. The dextran solution was made by a mixture of several different molecular weights from 6,000 to 500,000 Da.

After the active selective layer has been formed on the inner surface of the fiber, the intrinsic properties of PRO-PEI HF membranes, such as water and salt permeability, were tested in RO-mode by using a laboratory scale cross-flow filtration unit at ambient temperature. The hydraulic pressure varied from 5 to 22 bar was applied on the lumen side of the membrane modules. Water permeability coefficient (A) can be obtained using DI water as the feed at variable pressure. The salt rejection experiment was carried out using a 2000 ppm salt solution (~0.034 M NaCl solution) based on conductivity measurements (Mettler Toledo) of permeate and feed water at variable pressure. Details can be found elsewhere [17].

Mechanical properties of the hollow fiber substrates were assessed in term of tensile modulus, stress at break, strain at break, and burst pressure. The tensile modulus, stress and strain at break were performed using a Zwick 0.5 kN Universal Testing Machine at room temperature. To test the membrane burst pressure, two hollow fiber modules were made.

Every module consisted of fifteen fibers with an effective length of 22 cm. Interfacial polymerization of polyamide was carried out prior to the test. A hydraulic pressure at the interval of 2.5-5 bar was applied on the lumen side of the membrane modules until the fibers burst.

Inner surface topography and mechanical properties of PRO hollow fiber membranes were studied using an atomic force microscope (AFM, NX10, Park Systems). Loading forces of 5-50 μN were applied on the inner surface of three hollow fiber membranes: substrate, TFC-PEI, and TFC-PEI after long term PRO testing to assess the change in the mechanical properties before and after exposure to high pressure.

The porosity of PEI hollow fiber substrate was determined using gas pycnometer (Ultrapyc 1200e, Quantachrome, USA). Certain amounts of sample with known apparent volume were put into the sample chamber. High purity compressed nitrogen gas was used for measurement of sample's true volume. Porosity (P) can be calculated by:

$$P = \left(1 - \frac{V_T}{V_A} \right) 100\% \quad (1)$$

where V_T is true specific volume (cm^3/g) and V_A is apparent specific volume (cm^3/g).

2.4. Performance in PRO process

The schematic diagram of a laboratory scale PRO unit used in this study is similar to our previous work [12]. The orientation of the hollow fiber module for the reported data is active layer facing draw solution, unless otherwise stated. Since the active selective layer is on the inner surface of the fiber, the pressurized draw solution was pumped through the fiber lumen

by using a high pressure diaphragm pump. Pressure regulator valve and back pressure regulator were used in the draw solution loop for adjusting the pressure and the flow rate. Upstream and downstream pressures for draw solution are described as P_1 and P_2 , respectively, which can be monitored on a computer. Hydraulic pressure ranging from 5 to 22 bar was applied in the draw solution side. A concentrated salt solution was used to dose the draw solution to compensate the dilution of the draw solution during the experiments. It was controlled by the change in conductivity of the draw solution. Recirculation chillers connected to a submerged coil tube in the draw solution tank was used to remove heat generated by the high pressure pump. The temperature of the draw solution is maintained constant at 23 ± 1 °C. A 1.0 M NaCl solution was used as the draw solution. The feed solution was circulated using a peristaltic pump with a flow transmitter connected to a computer for flow rate adjustment. Dosing feed is controlled by the weight changing of the feed solution. The setup, thus, ran on the constant volume of feed. DI water was used as the feed water unless otherwise stated. The conductivity and temperature of the feed and draw solutions were monitored by probes connected to a data logging system. The flow rates of feed and draw solutions were maintained constant at 1.0 ± 0.05 L/min and 0.2 ± 0.05 L/min, respectively, throughout PRO testing. All PRO tests were conducted at temperature of 23 ± 1 °C.

Water flux (J_v) during PRO process through a semi-permeable membrane can be quantified by the volume change of the dosing feed (ΔV_{DF}) in a predetermined time interval (Δt).

$$J_v = \frac{\Delta V_{DF}}{A_m \Delta t} \quad (2)$$

where A_m is the effective membrane area of the hollow fiber membrane.

The salt flux (J_s) was determined by the change in the total amount of salt in the feed water in a certain time interval per membrane area [17].

$$J_s = \frac{\Delta(c_F V_F)}{A_m \Delta t} \quad (3)$$

where c_F is the salt concentration in the feed water tank based on the conductivity; V_F is the volume of the feed water. The power density (W) is determined by the water flux (J_v) and the corresponding hydraulic pressure difference over the membrane (ΔP).

3. Results and discussion

3.1. Substrate characteristics

The hollow fiber membrane substrate was fabricated by the NIPS method. It has an asymmetric structure as depicted in [Figure 1](#). It is shown that the dense skin on the inner surface is supported by a highly porous sublayer. The substrate has a fully sponge-like structure providing an excellent mechanical strength to withstand hydraulic pressure during PRO operation. Sponge-like structure, however, contributes to a severe ICP attributable to its lower porosity and higher tortuosity. Consequently, lower PRO water flux could be expected because of lower effective driving force. Therefore, an effort has been made to compensate for the membrane structure by reducing the thickness of the membrane wall. As seen in [Figure 1 A1](#), the substrate has a uniform wall thickness of $101 \pm 3 \mu\text{m}$. Reducing wall thickness, however, would weaken the mechanical strength of the membrane. Hence, the hollow fiber membrane in the current study was designed to possess a significantly smaller outer and inner diameter of $628 \mu\text{m}$ and $427 \mu\text{m}$, respectively. The properties of PEI hollow fiber substrates are given in Table 1.

Figure 1 Morphologies of PEI hollow fiber membrane substrate: (A1) cross-section; (A2) cross-section near the inner surface; (A3) inner surface; thin film composite (TFC) – PEI hollow fiber membrane before PRO testing (B1) cross-section; (B2) cross-section near the inner surface; (B3) inner surface

The PEI substrate has a pure water permeability (PWP) of 260 L/m².h.bar and a porosity of 73%. The MWCO of the inner surface is bigger than 500 kDa. The mechanical properties of the PEI hollow fiber substrate are summarized in Table 2. The membrane has a tensile modulus of 159 MPa as compared to 248 MPa for the previous PEI hollow fiber membrane. The stress and strain at break, representing stretch resistance and ductility respectively, are comparable to those of the previous PEI hollow fiber membrane. However, the current PEI membrane has much higher burst pressure of up to 24 bar.

The stretching stress, σ_s , on the inner surface of the hollow fiber membrane is given by [14]

$$\sigma_s = \left(\frac{\left(\frac{2t}{ID} + 1 \right)^2 + 1}{\left(\frac{2t}{ID} + 1 \right)^2 - 1} + \mu \right) P \quad (4)$$

where t and ID are the wall thickness and inner diameter of the hollow fiber membrane, respectively. μ is Poisson's ratio and P is the hydraulic pressure applied in the lumen side of the fiber [17]. Based on the calculation using equation (4), the previous PEI hollow fiber had a ratio of thickness over ID of 0.15, and thus the stretching stress at 16.5 bar is 70 bar. The current PEI hollow fiber has a ratio of thickness over ID of 0.24. The current fiber has similar stretching stress of 70 bar at a higher hydraulic pressure of 23 bar. The stretching stress increases as the ratio of thickness over diameter decreases. Consequently, the previous PEI fiber has a lower burst pressure.

Table 1 Properties of PEI hollow fiber membranes

Sample	Dimensions				Porosity (%)	PWP (L/m ² .h.bar)	MWCO (KDa)	Reference
	OD (μ m)	ID (μ m)	Thickness (μ m)	Thickness /ID				
PEI HF	628 $\pm$ 4	427 $\pm$ 6	101 $\pm$ 3	0.24	73 $\pm$ 3	260 $\pm$ 4	>500	Current work
PRO-PEI	1260	975	143	0.15	72 $\pm$ 2	360 $\pm$ 10	321 $\pm$ 30	[17]
PRO-PES	1380	980	200	0.20	80	273	45	[12]
FO-#C-PES	1370	960	205	0.21	82	278	39	[16]

Table 2 Mechanical and structural properties of PEI hollow fiber membranes

Sample	Tensile modulus (MPa)	Stress at break (MPa)	Strain at break (%)	Burst pressure –lumen* (bar)	Structural parameter (μ m)	Reference
PEI HF	159 $\pm$ 9.8	8.8 $\pm$ 0.3	39 $\pm$ 7.9	23.5	527	Current work
TFC-PEI	248 $\pm$ 8.0	8.6 $\pm$ 0.3	38.5 $\pm$ 4.0	16.5	610	[17]
TFC-PES	103	5.6	66.6	9.5	460	[12]
FO-#C-TFC	93	4.0	47.3	5.0	550	[16]

** Applied pressure from the lumen where the membrane lose its selectivity*

3.2. Morphology of composite PRO hollow fiber membranes

A polyamide selective layer can be interfacially polymerized onto the surface of a membrane. A number of commercial products have been developed based on this technique due to their high flux and salt rejection [20]. In this study, TFC and MPD have been used as the monomers to develop the polyamide RO-like skin on the inner surface of the PEI hollow fiber substrate. **Figure 1 B2** shows the cross-section near the inner surface of the hollow fiber membrane. The polyamide layer can be seen as an extra layer on the top of the porous support. **Figure 1 B3** shows that the inner surface was covered uniformly by the typical ridge and valley morphology. The same surface morphology has been reported in the literature [9, 16, 17].

The morphologies of TFC-PEI hollow fiber membranes after PRO testing are shown in **Figure 2**. It can be seen that the typical ridge and valley structure has flattened due to compaction as compared to and **Figure 1 B2** before PRO testing. With higher operating pressures and longer testing processes (eg. 200 h), the TFC layer became more compacted (**Figure 2 a3**). These SEM images were taken on randomly chosen parts of the membranes. The pictures presented can be taken as representatives for each sample.

Figure 2 Morphologies of thin film composite (TFC) – PEI hollow fiber membrane: (a) cross-section near inner surface and (b) polyamide layer on the inner surface, after PRO testing at different hydraulic pressures: (1) 12.5 bar; (2) 15.0 bar; (3) 22.0 bar; (4) 12.5-18.0 bar for 180 h

3.3. Intrinsic properties of PRO hollow fiber membrane

The initial PRO tests were performed to evaluate the membrane performance with regard to the burst pressure by applying hydraulic pressure on the draw solution side from 5 to 24 bar with membrane oriented with the active layer facing the draw solution. These experiments tested the PRO water flux and power density as a function of operating pressure as shown in **Figure 3**. The burst pressure was observed to be around 23.5 bar. Theoretically, the effective driving force across the active layer should decrease as the hydraulic pressure increases resulting in a decrease in PRO water flux, as previously reported [12, 14, 21]. Indeed, the flux decreased as expected in the low pressure range (5-15 bar). Interestingly, there is a turning point where the water flux started to increase as the pressure exceeded 15 bar. This phenomenon was also reported by Chou, *et al.* when a relatively stable PRO water flux was observed with increasing pressure [17] .

Figure 3 PRO water flux (Δ) and power density (□) of the TFC-PEI hollow fiber membrane at various operating pressures from 5 to 24 bar. Testing conditions: 1.0 M NaCl solution as the draw solution and DI water as the feed water at ambient temperature.

Since PRO water flux is closely associated with the water permeability of the membrane (A), following experiments have been designed to study the intrinsic properties of the membrane when the membrane was pressurised beyond the turning point (18 bar) and at the turning point (15 bar).

The permeation properties such as water permeability (A) and salt rejection were measured in pressure driven RO-mode in a cross-flow cell. The experiments were performed at different pressures. The ascending pressures were carried out from 5 to 18 bar and the descending pressure from 18 to 5 bar. The experimental results are shown in [Figure 4](#) . It can be seen that the water permeability increased from 3.3 to 5.3 L/m².h.bar as the pressure increased from 5 to 18 bar. However, when the pressure was decreased back to 5 bar, the water permeability remained stable at around 5.1 L/m².h.bar. This might due to physical deformation of the fibers at high pressure. As the membrane has been compacted, the polyamide selective layer becomes thinner (as shown in [Figure 2](#)), at the same time, the free volume of the polyamide layer may increase, leading to an increase in the water permeability of the membrane. Similar phenomenon has been discussed in the literature [17, 22]. It is shown that an excellent salt rejection of >98% could be sustained over the entire testing period, despite increasing the operating pressure. This also indicates that the ratio of salt permeability over water permeability (B/A) was maintained constant at 0.09 ± 0.02 bar against various hydraulic pressures.

Figure 4 Water permeability A (□), salt permeability B (■), B/A (●) and NaCl rejection (▲) as a function of hydraulic pressure of the feed, which implies the creeping occurred at 18 bars. Testing conditions: 2000 ppm NaCl solution as the feed at ambient temperature, operating pressure of 5-18 bar.

Similar testing of the membrane permeation properties was performed at a lower pressure range of 5 to 15 bar. It is interesting to see that the water permeability, A, is stable at around 4 L/m².h.bar as shown in [Figure 5](#). When the fiber was tested at the maximum pressure near the turning point, the stretching stress on the membrane matrix is less damaging. In this range, the membrane is also able to maintain high salt rejection (> 98%) and low salt permeability (B).

Figure 5 Water permeability A (□), salt permeability B (■), B/A (●) and NaCl rejection (▲) as a function of hydraulic pressure of the feed. Testing conditions: 2000 ppm NaCl solution as the feed at ambient temperature, operating pressure of 5-15 bar.

3.4. PRO performance

Further PRO experiments were conducted to evaluate the effects of the maximum operating pressure on the water flux, specific salt flux and power density. A short comparison of PRO performance between current work and reported work is shown in Table 3. It can be seen that the newly developed membrane has similar or better performance as compared with previous works, and shows proven strong mechanical strength. In each experiment, the membranes were pressurized from low to maximum pressure and back to low pressure. This was considered as one cycle. Each module tested underwent two cycles of ascending and descending pressure.

Table 3 Comparison of PRO performance

Salty water	Fresh water	Operation pressure ΔP (bar)	Water flux J_v (LMH)	Power density W (W/m ²)	Specific salt flux J_s/J_w (g/L)	Membrane	Reference
1.0M NaCl	DI water	15.0	48.5	20.2 (10 hrs testing)	-	TFC-PEI HF	Current work
1.0M NaCl	1 mM NaCl	15.1	49.9	20.9	1.7	TFC-PEI HF	[17]
	10 mM NaCl	15.1	44.7	18.7	1.7		
1.0M NaCl	10 mM NaCl	8.4	47.2	11.0	-	TFC-PES HF	[12]

The initial PRO test showed that the burst pressure is around 23.5 bar. Firstly, the membrane was challenged to the maximum pressure near the burst pressure. PRO results were summarized in Figure 6. When the pressure increased from 5 to 22 bar, it is shown in Figure 6 (a1) that the PRO water flux decreased and then increased again. At 22 bar, the PRO water flux and power density are 50 L/m².h and 29 W/m², respectively. The pressure was subsequently decreased to 5 bar. Since the membrane has been significantly compressed, the water flux at 5 bar increased by 46% from 50 to 73 L/m².h. As a result, the power density was also increased. However, the specific salt flux (J_s/J_v) shows good stability over the first whole cycle. On the second cycle, the membrane was pressurized from 5 to 22 bar. It can be seen that the water flux decreased significantly and peak power density was shifted to 15 bar pressure. During the ascending part of second cycle, the membrane showed a dramatic increase in the specific salt flux as the pressure increased from 5 to 20 bar. This indicates that the membrane selective layer has been damaged. As expected, the membrane burst at 20 bar.

Figure 6 (a) water flux (J_v) and J_s/J_v and (b) power density as a function of hydraulic pressure of the draw solution. One cycle consists of ascending ($\bullet$, $\blacktriangle$, $\blacksquare$) and descending ($\circ$, $\triangle$, $\square$) pressure. (1) and (2) are first and second cycle, respectively. PRO testing conditions: 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature; maximum pressure is 22 bar

On the other hand, at a lower maximum pressure, two pressure cycles could be completed without bursting as showed in Figure 7. Similar to the previous test, the PRO water flux increased after the membrane was pressurized at 20 bar during the first cycle. The flux turning point is around 15 bar. During the second cycle, the ascending and descending pressure curves were very closely matched. It is also shown that the membrane possesses identical peak power density of 28 W/m^2 at 20 bar. There was a slight increase in the specific salt flux during the second cycle when the membrane was pressurized at 20 bar. And the membrane lost its selectivity when tested under 1 bar using 500 ppm NaCl solution after the PRO test. The two tests show that the creeping is highly dependent on pressure. When the applied pressure was higher than the safe operation limit, membrane creeping will occur. And

the creeping is more severe when the applied pressure is higher as the membrane pressurized under 22 bar cannot survive the second cycle.

Figure 7 (a) water flux (J_v) and J_s/J_v and (b) power density as a function of hydraulic pressure of the draw solution. One cycle consists of ascending ($\bullet$, $\blacktriangle$, $\blacksquare$) and descending ($\circ$, $\triangle$, $\square$) pressure. (1) and (2) are first and second cycle, respectively. PRO testing conditions: 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature; maximum pressure is 20 bar

After PRO tests were completed, the module was opened and the hollow fiber membranes were subsequently viewed under the SEM to examine the membrane morphology after high pressure PRO tests. As depicted in Figure 8, the active layer of polyamide is delaminated (broken) after testing at the maximum pressure of 22 bar. Referring to the initial morphology of polyamide in Figure 1 B3, the active layer of polyamide was significantly compressed after pressurizing at 20 bar (shown in Figure 8b). It is obvious that pre-conditioning the membrane by compacting at high pressure results in an increase in water flux and power

density. However, further testing is needed to determine the ability of the membrane to endure the stress for a long period of time, which is to be discussed in the following section.

Figure 8 Surface morphologies of thin film composite (TFC) – PEI hollow fiber membrane after PRO testing at maximum pressures of 22 and 20 bar

3.5. Stability test

Stability tests were performed to evaluate the membrane behaviour over long term testing at high pressure. Briefly, hydraulic pressures of 12.5 (below turning point), 15.0 (turning point) and 18.0 bar (above turning point) were applied on the draw solution side. For each operating pressure, the membrane was run continuously for at least 60 h. This provides an insight into the optimum pressure for the PRO membrane and the behaviour of the membrane under continuous high pressure conditions.

Figure 9 shows a representative curve of power density, water flux, the specific salt flux and pressure with time at three different pressures. As can be seen from the figures, the

membrane performance is stable for more than 60 h, with the power density, water flux and specific salt flux at $15.7 \pm 0.3 \text{ W/m}^2$, $45 \pm 0.9 \text{ L/m}^2 \cdot \text{h}$ and $0.01 \pm 0.001 \text{ M}$, respectively, when the hydraulic pressure was set at 12.5 bar (below the flux turning point).

Figure 9 Power density and water flux (●, ▲, ■) and hydraulic pressure of the draw solution (○, △, □) as a function of time. PRO testing was performed continuously using 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature at hydraulic pressures of 12.5 (○), 15 (△) and 18 (□) bar.

When the pressure was increased to 15 bar, the power density increased to 19.2 W/m^2 . A slight increase in water flux was observed. This result shows that the applied pressure of 15 bar is the utmost pressure before the membrane starts to experience a creeping phenomenon. After 60 h running continuously, the pressure was increased to 18 bar which is above the turning point but it is still considerably lower than the burst pressure. It can be seen that there is a rapid increase in power density and water flux for the first 24 h. The membrane possesses an initial power density of 21 W/m^2 and PRO water flux of $43 \text{ L/m}^2 \cdot \text{h}$ at the operating

pressure of 18 bar. After 24 h, the power density and water flux of the membrane are stabilized at 27 W/m² and 54 L/m².h, respectively. As can be seen from [Figure 9](#), the membranes are able to maintain the specific salt flux as low as 0.01 M throughout 200 h PRO testing. In addition, the water flux of the membrane increased significantly when the pressure is reduced to lower pressure. The same modules were then tested in RO-mode by using a laboratory scale cross-flow filtration unit. It was interesting to observe that the membrane lost its selectivity to NaCl. This implied that membrane creeping due to high pressure loading might induce irreversible damage to the membrane. As such, an integrity test should be conducted to find out the safe operation pressure for the PRO hollow fiber membranes.

Nanoindentation is an effective and powerful tool to evaluate polymer creeping in term of Young's modulus, hardness, etc [23]. In this study, nanoindentation was performed by using AFM. The tip was pushed into the surface of the membrane at certain force to investigate the mechanical behaviour of the membrane matrix. Four loading forces ranging from 5 to 50 μ N were applied on the inner surface of three different membranes (PEI substrate, TFC-PEI before compaction, TFC-PEI after long term PRO testing) as shown in [Figure 10](#). When the loading force of 50 μ N was applied, the indent depths of the membrane are ~0.2, 0.7 and 1.3 μ m for substrate, TFC-PEI before compaction and TFC-PEI after PRO testing, respectively. The indent depth of 0.7 μ m for TFC-PEI before compression can be explained from [Figure 1 B3](#). The thin film cross-section is very porous and thus, can be compressed easily [14]. Therefore, the indent depth is a combination of the thin film layer and the substrate. In contrast, the TFC-PEI hollow fiber after long term exposing to high pressure might become very soft. This is confirmed by the indent depth of 1.3 μ m.

Figure 10 Atomic force microscope (AFM) images showing measured topography after indentation tests on the inner surface of hollow fiber membranes: (a) PEI substrate, (b) TFC-PEI, (c) TFC-PEI after long term PRO testing

From the data obtained through AFM, the hardness of the membrane can be calculated by Oliver-Pharr model [24]. The PEI hollow fiber substrate and TFC-PEI before compaction have similar hardness of 68 and 59 MPa, respectively. After long term PRO testing at high operating pressure, the hardness of the hollow fiber membrane drops significantly to 5.2 MPa. These facts are consistent with the experimental PRO testing in which the membrane selective property deteriorated and the fibers bursted easily.

In the real PRO operation, applied pressure will be relieved intermittently for backwashing to remove foulants. As such, an intermittent pressure should be applied to assess the integrity of the membranes after the pressure loading. And this intermittent test could be considered as a good approach to justify the membrane integrity. In the experiment, the pressure was gradually increased until 15 bars and maintained for about 8 hours, after which the pressure was gradually removed until 0 bars. Another cycle was conducted again after 10 hours, and

the results of water flux, specific salt flux and power density are summarized in Figure 11. It can be seen that the cycles were closely matched, indicating that the membrane integrity was well maintained at 15 bar. This shows that the membrane is safe to operate at the flux turning point. As shown previously, the creeping occurred when the pressure reached 18 bar. For that reason, it could be pronounced that it is safe to operate hollow fiber membranes at or below flux turning point for real PRO applications.

Figure 11 (a) water flux (J_v) and salt flux over water flux (J_s/J_v); (b) power density and pressure as a function of time. PRO testing was performed using 1.0 M NaCl as draw solution and DI water as the feed at ambient temperature at maximum hydraulic pressure of 15 bar

In a PRO process, when the applied pressure is relatively low (below the operating limit or the compaction zone), some slight membrane compaction-related effects can be observed.

Figure 11 demonstrates that these effects are totally reversible. Time-dependent deformations of the membrane (creeping) will hardly be observed under these conditions as permanent deformation of the substrate does not occur when the operating pressures are low [25]. However, the creep zone is encountered when the applied pressure exceeds the mechanical limits of the substrate. Under these conditions, the membrane will start to creep over time. Deformation of the selective layer occurs as the mechanical support layer is unable to completely resist high pressure loadings. As the membrane gradually deforms and its mechanical properties deteriorate, it would eventually lose its functionality. A safe operating limit can be found in between these two zones. Successful and sustainable application of a PRO process thus depends on identifying and using an applied pressure that is compatible with the long-term, stable operation of the membrane, while also maximizing the energy density of the overall process.

4. Conclusions

Most of the PRO tests for lab-made hollow fiber membranes reported in the literature did not present long-term PRO testing results and there was almost no integrity check. Thus it is difficult to judge the suitability and potential of the resultant PRO membrane for practical PRO application. The current work is believed to be the first effort to investigate the creeping phenomenon of PRO hollow fiber membrane due to high pressure loading and to report PRO membrane performance over a long term test of 200 hours. The major findings of the work can be summarized as follows:

- Membrane creeping was clearly observed when a non-stop 200 hr PRO testing was conducted, where the water flux gradually increased at 18 bar. The creeping phenomena resulted in irreversible damage to the membranes as the membrane lost most of its selectivity after the testing under high operating pressure. **Nanoindentation**

by using AFM was applied to investigate the mechanical behaviour of the membrane matrix before and after experiencing the high pressure, which has been demonstrated to be an effective tool to verify the membrane creeping.

- A flux turning point (15 bar) was observed during the PRO testing, and it was proved to be safe to operate the hollow fiber membrane at or below the flux turning point through an intermittent PRO testing.
- Membrane creeping is dependent on both pressure and time. Membrane creeping occurs when the applied pressure exceeds the safe operation limit and the effect of high pressure will accumulate over time thus resulting in permanent deformation in creep zone.
- A stable power density of 19.2 W/m² at 15 bars was achieved while the membrane integrity is ensured.

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