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# An investigation of polymer dope and heating effects on hollow fiber membranes

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ABSTRACT

Hollow fiber membranes were made from two different dope solutions by using a dry-jet wet spinning process. One dope solution contains cellulose acetate (CA)/*N*-methyl-2-pyrrolidone (NMP) with a mass ratio of 20/80 and the other contains polysulfone (PS)/NMP with a mass ratio of 15/85. The hollow fiber membranes were heated in a water bath to investigate the effect of heat treatment. It was found that for the CA membranes, the pore size shrank due to the heat treatment as there was a decrease in permeation and an increase in protein rejection. The most dramatic change for the CA membranes occurred after being heated to 95°C, which resulted in an increase in bovine serum albumin (BSA) rejection to 99% while the permeation decreased to $39\,\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$. This is due to heating above the glass transition temperature (67–68°C) for CA. For the PS membranes, the pore size remained unchanged throughout the two heat treatments as the glass transition temperature is 185 °C. The PS membranes did however have a smaller pore size to begin with as is evident by the >99% rejection of BSA. The permeation declined more rapidly for the PS membranes compared to the CA membranes due to the more hydrophobic nature of the polymer.

*Keywords:* Hollow fiber membranes; Cellulose acetate; Polysulfone

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## 1. Introduction

Currently, about half of the world's population suffers from water shortages, and over the next 25 years, the number of people affected by severe water shortages is expected to increase fourfold [1]. For this reason, water purification will be an important topic of interest for years to come. Membranes possess the ability to treat water from a wide variety of sources and can produce water that is of higher quality than traditional water treatment processes. Therefore, membranes and membrane processes have gained much popularity in recent years. Furthermore, membrane performance has been consistently increasing while membrane cost has been consistently decreasing [2]. Ultimately, dwindling freshwater resources, more stringent water treatment standards, and the need to augment existing water supplies in growing urban areas are all driving factors for the expansion of membrane processes [3].

In aqueous separations, UF has been found to be a suitable process for macromolecular separations. Though several methods are available for the preparation of UF membranes, phase inversion has been

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found to be a versatile technique for asymmetric UF membrane preparation, because the casting solution and conditions can be varied widely to get a desired pore structure [4]. Most membranes are either configured as flat sheet or spiral-wound modules; however, the hollow fiber configuration is also important because it offers three major advantages: (1) hollow fiber modules have a much larger ratio of membrane area to unit volume compared to flat and spiral-wound modules, and hence higher productivity per unit volume of membrane module; (2) they are self-supporting which can be back-washed to recover the flux; and (3) they have good flexibility in the mode of operation [5].

Cellulose acetate (CA) and polysulfone (PS) are two of the most widely used polymers for the fabrication of UF membranes. This is due to the fact that CA membranes have the following advantages: moderate flux, high salt rejection properties, cost effectiveness, and a renewable source of raw material [4]. PS membranes are well known for their chemical resistance, durability, thermal stability, and mechanical properties [6,7].

Hollow fibers are fabricated via the wet and dry-jet wet spinning processes. These processes allow for many parameters to be controlled, such as the dope extrusion rate [8–11], the bore fluid flow rate [10,12], the composition and temperature of the coagulant [13,14], the length of the air gap [8,10,14], additives to the dope [5,15], and the fiber take-up speed [16]. Varying these spinning conditions changes the surface layer structure thus giving different permeation characteristics. The post-treatment of hollow fiber UF membranes has also been studied including heat treatment, hypochlorite treatment, and glycerol treatment [5,17,18]. Each of these post-treatment procedures is known to affect the hollow fiber characteristics.

This paper explores the effects of heat and glycerol post-treatment on the properties and morphology of CA and PS hollow fiber UF membranes, respectively.

## 2. Experimental

### 2.1. Materials

The polymers used for fabrication of the hollow fiber membranes were (CA, average $M_N$ 30,000) with acetyl content of 39.8 wt.% purchased from Sigma-Aldrich and PS (Udel P-1700 NT11) supplied by Solvay Advanced Polymers. The solvent, *N*-methyl-2-pyrrolidone (NMP, >99%) was supplied by Alfa Aesar. A mixture of acetone and deionized (DI) water was used as the bore fluid for spinning. The acetone (99.5%) was purchased from Fisher Scientific. DI water was supplied by a continuous distillation apparatus. Bovine serum albumin (BSA, MW 66,000) and Lipase from porcine pancreas, Type II were both purchased from Sigma–Aldrich and were used to characterize the performance of the hollow fiber UF membranes. Glycerol (⩾99%) from Acros Organics was used in the post-treatment of the UF hollow fiber membranes.

### 2.2. Preparation of polymer dope and hollow fiber fabrication

The dope solution for spinning was prepared by adding CA powder or PS pellets to *N*-methylpyrrolidone (NMP) to form a 20 and 15 weight percent dope respectively. Each mixture was then stirred in a flask covered with para-film for at least 24 h to ensure the dope was a true homogenous solution. Finally, the dope solution was placed in a metal canister and was degassed for at least 1 h to remove any gas bubbles prior to spinning.

The CA and PS hollow fiber membranes were fabricated using the well-known dry-jet wet-spinning process [16,19–21]. A mixture of 90/10 wt.% water/acetone was used as the bore fluid. The dope solution and bore fluid were each fed into the spinneret by means of pressure from a nitrogen gas cylinder. The flow rates of the dope solution and bore fluid were regulated using valves and by referencing the previously collected calibration data in Table 1 for each corresponding dope. Tap water at room temperature

Table 1
Flow rate calibration data

| Dope: CA/NMP 20 wt.% | | | Dope: PS/NMP 15 wt.% | | |
|---|---|---|---|---|---|
| Pressure (psi) | Flow rate (mL/min) | Flow quality | Pressure (psi) | Flow rate (mL/min) | Flow quality |
| 30 | 0.15 | Drips | 5 | 0.77 | Drips |
| 40 | 0.23 | Drips | 10 | 1.65 | Drips |
| 50 | 0.31 | Almost consistent | 15 | 2.50 | Drips |
| 60 | 0.42 | Consistent | 20 | 3.50 | Drips |
| 70 | 0.55 | Consistent | 25 | 4.30 | Drips |

Table 2
Process parameters and spinning conditions

| Dope solution (wt.%) | CA/NMP (20:80) | PS/NMP (15:85) |
|---|---|---|
| Dope flow rate (mL/min) | 0.55 | 1.3 |
| Bore fluid composition (wt.%) | Water/acetone (90:10) | Water/acetone (90:10) |
| Bore fluid flow rate (mL/min) | 0.65 | 0.6 |
| Air gap (cm) | 8 | 8 |
| Draw speed | Free fall | Free fall |
| External coagulant | Water | Water |
| Dimensions of spinneret (mm) | i.d./o.d. (0.5/0.8) | i.d./o.d. (0.5/0.8) |

was used as the external coagulation bath. The detailed spinning conditions are summarized in Table 2. The nascent hollow fiber membranes were then immersed in DI water for several days to remove any residual solvent.

### 2.3. Heat-treatment of the hollow fiber membranes

After the phase inversion and residual solvent water wash, the hollow fiber membranes were divided into three groups for heat treatment. The first group of membranes (designated as either CA-1 or PS-1) was not subjected to any heat treatment. The second group (designated as either CA-2 or PS-2) was immersed in a water bath at 60°C for 1 h. Then, the fibers were cooled by transferring them to a water bath at room temperature. The third group (designated as either CA-3 or PS-3) was heat-treated in two steps. First, the fibers were immersed in a water bath at 60°C for 1 h followed by immersing them in a water bath at 95°C for 20 min. Finally, the fibers were cooled by transferring them to a water bath at room temperature. After cooling, all fibers were placed in a 50 wt.% glycerol solution for 24 h and air-dried at room temperature prior to making membrane modules.

### 2.4. Characterization of hollow fiber ultrafiltration membranes

The experiments to measure flux, permeability, and retention of hollow fiber UF membranes were carried out at room temperature in a cross-flow filtration setup as shown in Fig. 1. Test modules were made by placing two fibers with an effective length of 30 cm in Nylon tubing (1/4´´ Dayco Nylo-Seal) with a JACO ¼´´ tee on each end. The fibers were sealed into the tubing by surrounding them with cotton and then epoxy adhesive (3M Scotch-Weld Structural Plastic Adhesive DP-8005) to ensure a watertight seal. The cotton was placed around the fibers to guarantee that the epoxy would not travel past the tee.

The membrane modules were first tested for pure water permeability (PWP) by feeding DI water on the shell side of the fibers and collecting permeate at the end of each fiber in 10 min increments over a 2 h time span. Then, the fibers were subjected to 2 h of filtration of a BSA solution (1 g/L) taking permeation readings every 10 min followed by 2 h of filtration of a lipase solution (1 g/L). The absorbance of the protein feed solutions as well as all of the protein permeate samples were measured using a Shimadzu UV-vis Recording Spectrophotometer (UV-2401 PC) at a wavelength of 270 nm. The shell side pressure for all filtration experiments was in the range of 239–294 kPa (20–28 psig) and the average pressure was taken for all permeation calculations. The permeation and percent retention were calculated by using Eqs. (1) and (2) respectively.

$$\mathrm{PWP} = \frac{Q}{A\Delta P} = \frac{Q}{n\pi D_{\mathrm{i}} L\Delta P} \tag{1}$$

where $Q$ is the volumetric flow rate of permeate ($\mathrm{L\,h^{-1}}$), $A$ is the hollow fiber membrane area ($\mathrm{m^2}$), $n$ is the number of fibers, $D_{\mathrm{i}}$ is the inner diameter of the hollow fiber (m), $L$ is the length of the hollow fiber (m), and $\Delta P$ is the shell side pressure (bar).

$$\text{retention}\,(\%) = \left(1 - \frac{A_{\mathrm{p}} - A_{\mathrm{f}}}{A_{\mathrm{f}}}\right) \times 100 \tag{2}$$

where $A_{\mathrm{p}}$ and $A_{\mathrm{f}}$ represent the absorbance of the protein in the permeate and feed, respectively.

For scanning electron microscopy (SEM) analyses, the fiber samples before and after heat-treatment were immersed in liquid nitrogen to break the membranes into clean cross-sections. The fibers were then coated with a thin layer of palladium-gold using a Cressington 108 Auto sputtering device. To investigate the

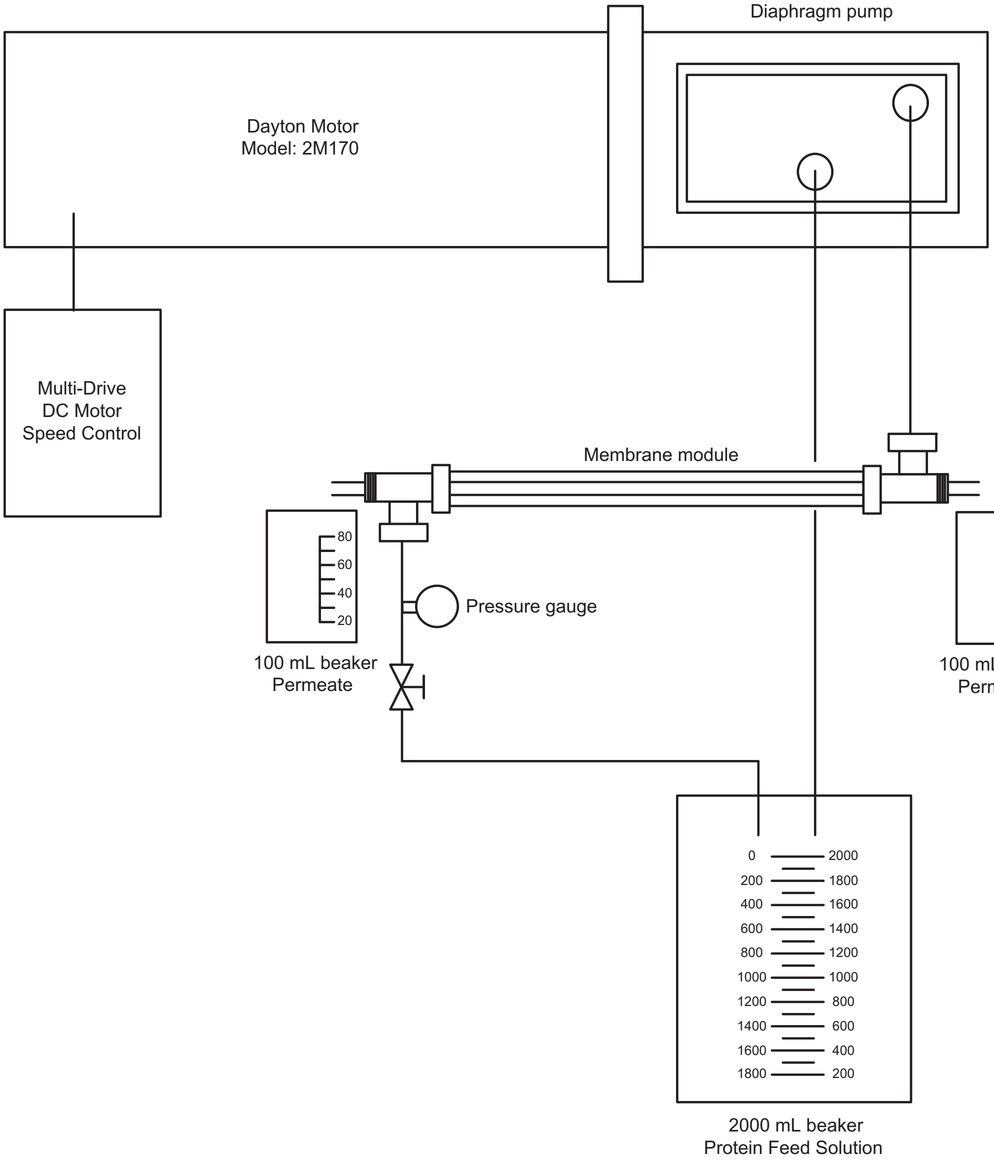

Fig. 1. Schematic diagram of the experimental setup for the ultrafiltration experiments.

cross-section, structure, and morphology of the fibers, these samples were studied using a Hitachi S-4800 SEM.

## 3. Results and discussion

### 3.1. Effect of heat treatment and glycerol treatment on membrane morphology

SEM was used to investigate the morphology and structure of the hollow fiber membranes. The SEM images of the cross-section of CA and PS membranes are shown in Fig. 2. The macrovoids visible in the sublayer structure of the CA membranes (a–c) detract from the overall effectiveness of the filtration performance of the membrane. Research has been done that shows that the addition of an additive to the dope such as polyvinyl pyrrolidone (PVP) would have favored the suppression of such macrovoids [5,7,22]. The formation of the multiple layers as is more clearly seen in Fig. 2 (d–f) is due to the combined effect of the internal coagulant (acetone/water bore solution) and the external coagulant (water). The inner surface and sublayer are known to be highly porous when compared to the dense outer skin. This phenomenon is illustrated in Fig. 3 in which the dense outer skin is on the left side of the cross-section image and the more porous inner surface is on the right side. This is

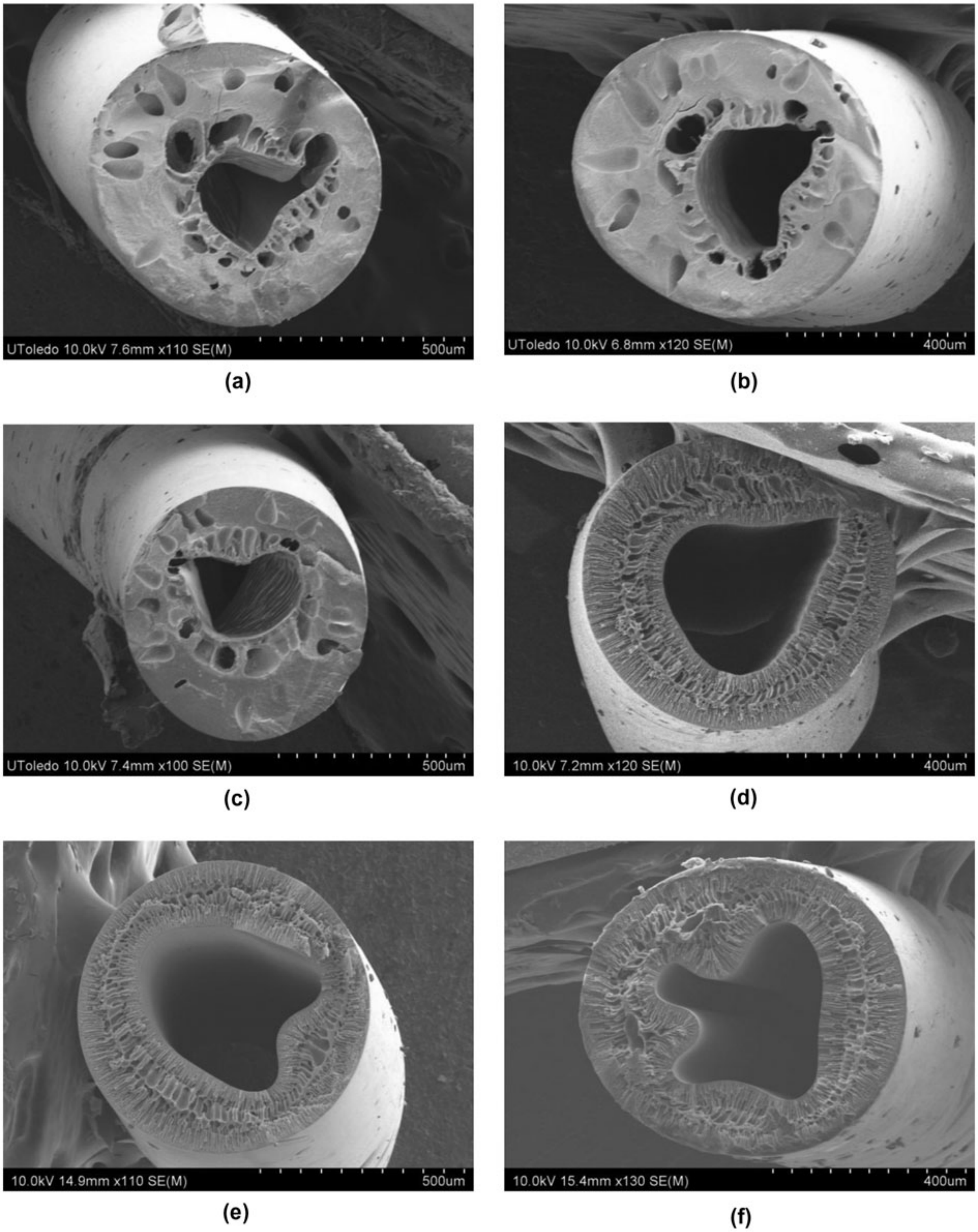

Fig. 2. Overall cross-section of CA and PS hollow fiber membranes with different heat treatments: (a) CA-1, no heat treatment, (b) CA-2, heat treated to 60°C, (c) CA-3, heat treated to 60°C, and then to 95°C, (d) PS-1, no heat treatment, (e) PS-2, heat treated to 60°C and (f) PS-3, heat treated to 60°C, and then to 95°C.

due to the delayed phase inversion caused by using a mixture of acetone and water as the bore fluid in the spinning process [18]. The dense outer skin is the result of using water as the external coagulant in

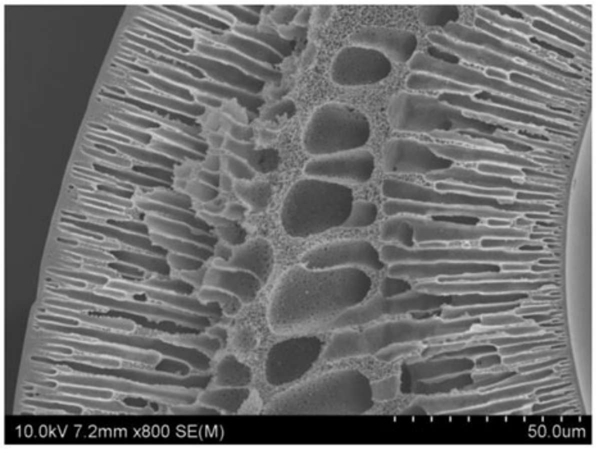

Fig. 3. Partial cross-section magnification of PS-2 hollow fiber.

Table 3
PWP and protein rejection of the CA and PS hollow fiber membranes

| Membrane ID | PWP ($\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$) | BSA rejection (%) | Lipase rejection (%) |
|---|---|---|---|
| CA-1 | 103.72 | 80.54 | 69.19 |
| CA-2 | 95.13 | 78.17 | 67.66 |
| CA-3 | 45.93 | 98.91 | 73.87 |
| PS-1 | 63.90 | 99.50 | 68.51 |
| PS-2 | 48.10 | 99.00 | 71.65 |
| PS-3 | 54.38 | 99.55 | 67.17 |

spinning as the phase inversion occurs immediately once the fibers enter the coagulant.

The glycerol solution did not have a noticeable effect on the surface structure or morphology of the hollow fiber membranes. It did however ensure that the fibers did not shrivel during the air drying step of making the membrane modules. There also was no appreciable change in the cross-sectional view between hollow fibers with and without heat treatment. It does appear that the inside surface of the CA hollow fibers remained smooth without a noticeable change until the second heat treatment step in which the temperature reached 95°C (Fig. 2(c)), at which temperature the surface became more rough. This could be better verified by taking more images of the inner surface of the CA membranes. This change in surface structure can be attributed to having heated the CA membranes past the glass transition temperature ($T_g$) of 67–68°C for CA. The PS membranes did not show any change in morphology as a result of the heat treatments as the glass transition temperature of PS is 185°C.

### 3.2. Membrane characterization through ultrafiltration

Table 3 gives the results obtained from the UF tests. At pressures of 2.4–3.1 bar (20–30 psig), the CA-1, CA-2, and CA-3 membranes had PWP values of 103.72, 95.13, and 45.93 $\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$, respectively. These are similar to values found in previous research done by Qin et al. [5] for similar CA UF hollow fibers. Their corresponding rejection values of BSA were 80.54, 78.17, and 98.91%, respectively, while their rejections values of Lipase were 69.19, 67.66, and 73.87%, respectively. This trend supports the idea that the heat treatment at 60°C only slightly affects the pores on the membrane surface whereas the heat treatment at 95°C has a much greater impact. At similar pressures, the PS-1, PS-2, and PS-3 membranes had PWP values of 63.90, 48.10, and 54.38 $\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$, respectively. Their corresponding rejection values of BSA were all near 100% emphasizing the fact that the pore sizes for the PS membranes are near the size of BSA molecules. There was no large distinction between the Lipase rejection results for the three PS membranes. The PWP data suggests that the heat treatment did very little to modify the pore structure of the membranes which would seem likely as the $T_g$ of PS is 185°C. The PWP data collected is considerably lower than that found by Qin et al. [7] due to not having blended another polymer such as PVP with the PS, which would have reduced the hydrophobicity of a pure PS membrane.

Heat treatment has been reported to be an effective way to modify the pore structural characteristics [18,23,24]. According to Su et al. [18], in the side chains of CA, most oxygen atoms of the carbonyl groups are intramolecularly hydrogen-bonded. After the hydrogen bonds absorb enough energy during the heat treatment process, they may be broken and the carbonyl groups have more freedom to rotate as single bonds. This enhances the possibility for the macromolecular chains or segments from different CA molecules to get closer with each other and form intermolecular hydrogen bonds [25,26]. A higher packing density of the CA macromolecular chains or segments thus results from the heat treatment.

### 3.3. Performance of the membranes in the ultrafiltration separation

To evaluate the performance of the UF membranes over time, the permeability was measured throughout the PWP, BSA and Lipase rejection tests totaling over

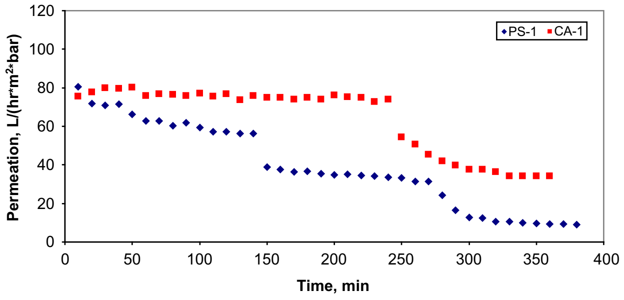

Fig. 4. Permeation data for PS-1 and CA-1 throughout the PWP, BSA, and Lipase rejection studies.

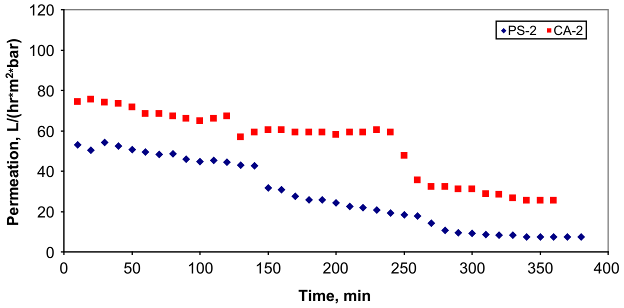

Fig. 5. Permeation data for PS-2 and CA-2 throughout the PWP, BSA, and Lipase rejection studies.

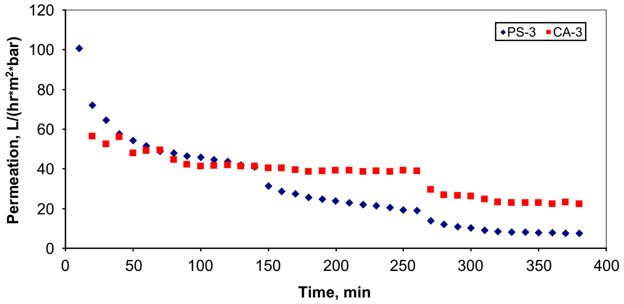

Fig. 6. Permeation data for PS-3 and CA-3 throughout the PWP, BSA, and Lipase rejection studies.

6 h of filtration data. It can be seen from Figs. 4–6 that the results of permeability for all six membrane modules tested followed a similar downward trend in permeability over time. All of the CA membranes had higher permeability in comparison to the PS membranes due to the hydrophilic nature of the polymer. The decrease in permeability for all fibers can most likely be attributed to the fouling of the membranes. One of the significant flux reduction mechanisms is concentration-polarization at the membrane surface. This phenomenon would lead to an increase in the osmotic pressure. Membrane fouling due to the adsorption of solute molecules on the membrane surface and in the pores would then occur [5].

## 4. Conclusions

CA and PS hollow fiber UF membranes were developed from dopes containing CA/NMP and PS/NMP with a mass ratio of 20/80 and 15/85 respectively. The experimental results showed that heat treatment at 60°C for 60 min had only a slight effect on the membrane structure. Further, heat treatment of the CA membranes at 95°C for 20 min resulted in a significant shrinkage of the pores on the membrane surface as it was evident by the increased BSA rejection and the decreased permeability. Heat treatment of the PS hollow fiber membranes up to 95°C had no significant effect on the permeability or pore size. Future work should focus on reducing the fouling tendency of the membranes as well as reducing the thickness of the inner sublayer to enhance the permeability while maintaining similar pore sizes.

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## References

[1] R. Engelman, R.P. Cincotta, B. Dye, T. Gardner-Outlaw, J. Wisnewski, People in the Balance: Population and Natural Resources at the Turn of the Millennium, Population Action International, Washington, DC, 2000, pp. 1–36.

[2] J. Birkett, R. Truby, A Figure of Merit for Appreciating Improvements in RO Membrane Performance, International Desalination Association News, vol. 16, 2007.

[3] Jana Safarik, Donald W. Phipps, Jr., Role of Microfiltration (MF) Cake Layer Composition and Stability in Desalination Efficiency, C.D.O.W. Resources, Sacramento, CA, April 2005.

[4] R. Malaisamy, R. Mahendran, D. Mohan, M. Rajendran, V. Mohan, Cellulose acetate and sulfonated polysulfone blend ultrafiltration membranes. I. Preparation and characterization, J. Appl. Polym. Sci. 86(7) (2002) 1749–1761.

[5] J.J. Qin, Y. Li, L.S. Lee, H. Lee, Cellulose acetate hollow fiber ultrafiltration membranes made from CA/PVP 360 K/NMP/water, J. Membr. Sci. 218(1–2) (2003) 173–183.

[6] D. Mockel, E. Staude, M.D. Guiver, Static protein adsorption, ultrafiltration behavior and cleanability of hydrophilized polysulfone membranes, J. Membr. Sci. 158(1–2) (1999) 63–75.

[7] J.-J. Qin, F.-S. Wong, Y. Li, Y.-T. Liu, A high flux ultrafiltration membrane spun from PSU/PVP (K90)/DMF/1,2-propanediol, J. Membr. Sci. 211(1) (2003) 139–147.

[8] A. Idris, M.Y. Noordin, A.F. Ismail, S.J. Shilton, Study of shear rate influence on the performance of cellulose acetate reverse osmosis hollow fiber membranes, J. Membr. Sci. 202 (1–2) (2002) 205–215.

[9] A.F. Ismail, M.I. Mustaffar, R.M. Illias, M.S. Abdullah, Effect of dope extrusion rate on morphology and performance of hollow fibers membrane for ultrafiltration, Sep. Purif. Technol. 49(1) (2006) 10–19.

[10] S.A. McKelvey, D.T. Clausi, W.J. Koros, A guide to establishing hollow fiber macroscopic properties for membrane applications, J. Membr. Sci. 124(2) (1997) 223–232.

[11] J. Qin, T.-S. Chung, Effect of dope flow rate on the morphology, separation performance, thermal and mechanical properties of ultrafiltration hollow fibre membranes, J. Membr. Sci. 157(1) (1999) 35–51.

[12] T.S. Chung, S.K. Teoh, X. Hu, Formation of ultrathin high-performance polyethersulfone hollow-fiber membranes, J. Membr. Sci. 133(2) (1997) 161–175.

[13] W.-L. Chou, M.-C. Yang, Effect of coagulant temperature and composition on surface morphology and mass transfer properties of cellulose acetate hollow fiber membranes, Polym. Adv. Technol. 16(7) (2005) 524–532.

[14] T.-S. Chung, E.R. Kafchinski, The effects of spinning conditions on asymmetric 6FDA/6FDAM polyimide hollow fibers for air separation, J. Appl. Polym. Sci. 65(8) (1997) 1555–1569.

[15] H.A. Tsai, D.H. Huang, S.C. Fan, Y.C. Wang, C.L. Li, K.R. Lee, J.Y. Lai, Investigation of surfactant addition effect on the vapor permeation of aqueous ethanol mixtures through polysulfone hollow fiber membranes, J. Membr. Sci. 198(2) (2002) 245–258.

[16] Y. Ming-Chien, C. Ming-Tze, Effect of post-drawing on the mechanical and mass transfer properties of polyacrylonitrile hollow fiber membranes, J. Membr. Sci. 116(2) (1996) 279–291.

[17] M. Gholami, S. Nasseri, C.Y. Feng, T. Matsuura, K.C. Khulbe, The effect of heat-treatment on the ultrafiltration performance of polyethersulfone (PES) hollow-fiber membranes, Desalination 155(3) (2003) 293–301.

[18] J. Su, Q. Yang, J.F. Teo, T.S. Chung, Cellulose acetate nanofiltration hollow fiber membranes for forward osmosis processes, J. Membr. Sci. 355(1–2) (2010) 36–44.

[19] T.-S. Chung, X. Hu, Effect of air-gap distance on the morphology and thermal properties of polyethersulfone hollow fibers, J. Appl. Polym. Sci. 66(6) (1998) 1067–1077.

[20] J.-J. Qin, J. Gu, T.-S. Chung, Effect of wet and dry-jet wet spinning on the shear-induced orientation during the formation of ultrafiltration hollow fiber membranes, J. Membr. Sci. 182(1–2) (2001) 57–75.

[21] K.Y. Wang, T.-S. Chung, Polybenzimidazole nanofiltration hollow fiber for cephalexin separation, AlChE J. 52(4) (2006) 1363–1377.

[22] Z.-L. Xu, T.-S. Chung, Y. Huang, Effect of polyvinyl pyrrolidone molecular weights on morphology, oil/water separation, mechanical and thermal properties of polyetherimide/polyvinyl pyrrolidone hollow fiber membranes, J. Appl. Polym. Sci. 74(9) (1999) 2220–2233.

[23] M.-J. Han, D. Bhattacharyya, Thermal annealing effect on cellulose acetate reverse osmosis membrane structure, Desalination 101(2) (1995) 195–200.

[24] B. Kunst, S. Sourirajan, Development and performance of some porous cellulose acetate membranes for reverse osmosis desalination, J. Appl. Polym. Sci. 14(10) (1970) 2559–2568.

[25] J.L. Halary, C. Noël, L. Monnerie, Analysis of transport phenomena in cellulose diacetate membranes IV. Dependence of membrane desalination properties on annealing temperature: A molecular analysis, Desalination 32 (1980) 65–76.

[26] H.H. Schwarz, K. Richau, H.G. Hicke, Annealing effect in porous cellulose acetate membranes, J. Membr. Sci. 34(3) (1987) 283–296.