ORIGINAL ARTICLE

Effects of dope extrusion rate on the morphology and gas separation performance of asymmetric polysulfone hollow fiber membranes for O_2/N_2 separation

Ahmad Fausi Ismail[1], Suhaina Mohd. Ibrahim[2] and Nor Shawal bin Nasri[3]

Abstract

Ismail, A.F., Suhaina, M.I., and Nasri, N.S.
Effects of dope extrusion rate on the morphology and gas separation performance of asymmetric polysulfone hollow fiber membranes for O_2/N_2 separation
Songklanakarin J. Sci. Technol., 2002, 24(Suppl.) : 833-842

The objective of this study was to investigate the influence of dope extrusion rates on morphology and gas separation performance of asymmetric polysulfone hollow fiber membranes. Asymmetric polysulfone hollow fiber membranes for gas separation were prepared from a solution consisting of 26.0 wt. % of polysulfone, 30.4 wt. % of N, N-dimethylacetamide, 30.4 wt. % of tetrahydrofuran and 13.2 wt. % ethanol. The dry/wet phase separation process was applied to a dry/wet spinning process. Fibers were spun at various dope extrusion rates (DER) ranging from 1.5 - 3.0 cm^3/min and hence at different levels of shear. The results suggest that as the dope extrusion rate is increased, the selectivity will increase until a critical level of shear is reached, beyond which the membrane performance deteriorates. Pressure-normalized-fluxes and selectivities were evaluated by using pure oxygen and nitrogen as test gases.

Key words : gas separation, polysulfone, shear rates, hollow fiber membranes

[1]Ph.D. (Chemical Engineering), Prof., [2]M.Sc. (Gas Engineering), Post graduate student, [3]Ph.D. (Gas Engineering), Assoc. Prof., Membrane Research Unit, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor, Malaysia.
Corresponding e-mail : afauzi@utm.my
Received, 9 January, 2003 Accepted, 2 July 2003

The development of hollow fiber membrane technology has been greatly inspired by intensive research and development of reverse osmosis membranes during the 1960s (Puri, 1990). However, the preparation of asymmetric hollow fiber membranes is more complex than that of flat sheet membranes because it involves many controlling parameters during spinning of hollow fiber (Chung *et al*., 2000 and Koros *et al*., 1993). Much of the previous work that has been published focused on the compositions and temperatures of the dope solutions (Pesek *et al*., 1994; Hachisuka *et al*., 1996; Torrestiana Sanchez *et al*., 1999), dope extrusion rates (McKelvey *et al*., 1997; Aptel *et al*., 1985), compositions, temperatures and flow rates of the bore fluid (McKelvey *et al*., 1997; Chung *et al*., 1998), compositions and temperatures of external coagulants (Pinnau *et al*., 1988; van't Hof *et al*., 1992; Henmi *et al*., 1993), and length and humidity of the air gap (McKelvey *et al*., 1997; Chung *et al*., 1998).

The rheological conditions such as the degree of shear and elongation experienced during membrane casting or hollow fiber spinning were found to alter the degree of molecular orientation in the skin layer of the asymmetric membranes. This phenomenon resulted in the enhancement of membrane selectivity beyond the recognized intrinsic value of the particular polymer (Ismail, 1997; Ismail *et al*., 1999).

A number of investigators have recognized the importance of a rheological perspective in membrane fabrication and performance. Some of them have systematically investigated these rheological effects with regard to gas separation and ultrafiltration membranes.

Aptel *et al*. (1985) have shown that orientation of polymeric macromolecules induced in the spinneret would influence the properties of dry-jet-wet spun ultrafiltration hollow fiber membranes. They found that increasing dope flow rate increased the shear stress and subsequently reduced the water flux. They kept the bore fluid rate constant over varying dope flow rates. However, the produced fiber diameter does not exhibit similar dimension.

East *et al*. (1986) have investigated the effect of polymer extrusion rates on dry-jet-wet spun polysulfone hollow fiber properties for gas separation and found that increasing dope extrusion rates reduced the gas permeation rates but enhanced the selectivity. They did not keep the ratios of dope to bore fluid rate constant.

Shilton *et al*. (1994 and 1996) have indicated that both gas permeability and selectivity were enhanced with increasing dope extrusion rates. The increase in selectivity was due to enhanced orientation in the skin of dry-jet-wet spun polysulfone hollow fibers. In their work, they have coupled both the shear and air gap effects in the fiber formation and their data analysis. In addition, since their spinning solution was a viscoelastic fluid, molecular orientation induced by shear stress within the spinneret might be relaxed in the air gap region if the elongation stress along the spinning line was small, or enhanced if the stress in the spinning line was high. Furthermore, they used water as an internal coagulant. Water was a very effective coagulant and it would probably result in the formation of a relatively dense inner skin. Therefore, it is possible that their hollow fibers might had two layers of relatively dense skins and it is uncertain what effects the elongated inner skin structure had on their mechanical properties and gas separation performance.

Ismail *et al*. (1997) have used plane polarized infrared spectroscopy to measure the molecular orientation in the active layer of dry-jet-wet spun polysulfone hollow fibers and demonstrated that there was an increased molecular orientation in high sheared membranes resulting in higher gas selectivity.

Chung *et al*. (2002) have found that, at low shear rates, the permeances of non-polar molecules such as H_2, O_2, N_2, and CH_4 decreased, while their relative selectivities increased with increasing shear rates. At a certain range of shear rate, all permeances increased with increasing shear rates, while their selectivities decreased. In low shear rate regions, the decrease in permeance or increase in selectivity with increasing shear rates arose from a better molecular orientation and

chain packing induced by shear. With increasing shear in high shear rate regions, the increase in permeance or decrease in selectivity was mainly attributed to relatively porous skin structures induced by the low viscosity nature of a power law spinning fluid at high shear rates. Their work suggested that there might exist an optimum shear rate to yield optimal membrane morphology for gas separation.

It has been acknowledged that in the spinning of textile fibers, the influence of rheologically induced molecular orientation on fiber properties will affect selectivity. Such effects have been observed in the performance of ultrafiltration and gas separation hollow fibers and are well documented (Aptel *et al*., 1985; Chung *et al*., 1998, 2000; Ismail *et al*., 1997, 1999; Pesek *et al*., 1994; Sharpe *et al*., 1999; Shilton *et al*., 1994, 1996, 1997 and so on). Therefore, in this paper, we report the study of the effects of dope extrusion rates on the morphology and gas separation performance of asymmetric polysulfone hollow fiber membranes for oxygen/nitrogen separation using our newly developed dope formulation by Yean (2002).

Experimental

Materials

In this study, the dope consisted of polysulfone in the pellets form (Udel bisphenol A polysolfone (Udel P1700)) supplied by Amoco Chemicals. The organic chemicals used in multicomponent spinning solution included: N, N-dimethylacetamide (DMAc) (less volatile solvents), tetrahydrofuran (THF) (highly volatile solvents), and ethanol (EtOH) (nonsolvent). The bore coagulant was a 20.0 wt. % solution of potassium acetate in water at ambient temperature. For coating materials, polydimethylsiloxane (Sylgard 184, Dow Corning) in n-hexane solution was used. Meanwhile, in the potting up of fiber modules, glue (Epoxy) was used. All of these organic chemicals were obtained from Chemical Store Center, Universiti Teknologi Malaysia.

Preparation of dope formulation

Asymmetric polysulfone hollow fiber membranes for gas separation were prepared from solution consists of 26.0 wt. % of polysulfone, 30.4 wt. % of N, N-dimethylacetamide, 30.4 wt. % of tetrahydrofuran and 13.2 wt. % ethanol (Yean, 2002).

Polysulfone was first dried in an oven at 60^{o}C overnight before use to remove absorbed water vapor. The compositions (by percentage weight) of each component were measured using a digital electronic balance. Solvents were initially fed into a flask, by the degree of volatility order, followed by the polymer, which was slowly added to prevent agglomeration. After the mixture had become homogeneous, nonsolvent was added. The mixture was stirred at about 55^{o}C throughout the mixing process to enhance dissolution of polymer yet preventing loss of solvents. The solution was then kept in a storage bottle and degassed to remove any micro bubbles in the solution.

Spinning of asymmetric hollow fiber membrane

Asymmetric polysulfone hollow fiber membranes for gas separation were fabricated using a dry/wet spinning process with forced convection in the dry gap. The dope was placed in a stainless steel dope reservoir (1 litre in volume) that was subsequently pumped to the tube in an orifice spinneret by a gear pump.

On extrusion from the spinneret (spinneret dimensions: OD 600 μm/ID 290 (m), the prenascent fiber passed through a cylindrical forced convection chamber (diameter 5 cm, height 9 cm), which was flushed with 4 l/min of nitrogen gas. The nitrogen was introduced through a tube (diameter 0.6 cm), which abutted upon the chamber, normal to the surface at mid height. This arrangement provided a controlled forced convective environment for inducing initial phase separation. Hollow fibers were spun at various dope extrusion rates and hence at different levels of shear. Dope extrusion rates in this study were set: 1.5, 2.0, 2.5, and 3.0 cm^{3}/min. The jet stretch

ratio (wind up speed/extrusion speed) was fixed at 1 throughout. The ratio of the dope extrusion rate to the bore fluid injection rate was also maintained at a constant value of 3.

The bore coagulant was a 20.0 wt. % solution of potassium acetate in water at ambient temperature (Ismail *et al*., 1999). Potassium acetate was added in water as to lower the water activity (Pesek and Koros, 1994; Ismail, 1997 and Sharpe *et al*., 1999). Tap water at 14±0.5°C was used in an external coagulation bath. The fiber filament was then passed through a series of rollers, first through the coagulation bath and then through a washing or treatment bath. The fully formed solid hollow fibers were continuously collected on a wind up drum, which had a diameter of 16 cm. The fibers were cut on the drum using a fresh razor blade to a suitable working length of 50 cm. The hollow fibers were rinsed in water for two days, and then immersed into methanol for solvent exchange for one day, and finally air-dried overnight at ambient temperature. Table 1 summarizes the general spinning conditions described above.

Gas permeation

The pressure-normalized fluxes of the fibers were measured for pure oxygen and nitrogen at room temperature at a pressure drop of 1 bar. The membranes were also tested after coating. Volumetric flow rates of permeate were measured by a soap bubble flow meter. Gas permeation rate through asymmetric membrane is usually expressed as

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{A\Delta p}$$

where P_i/l is defined as pressure-normalized flux or permeability for gas i (permeability coefficient divided by effective skin thickness) (cm^3 (STP)/cm^2.s.cmHg), Q_i is volumetric flow rate of gas i (cm^3/s), Δp is pressure difference across membrane (cmHg), A is membrane effective surface area (cm^2) and l is membrane skin thickness (cm). The common unit of pressure-normalized gas flux is *GPU* (1 *GPU* = 1×10^{-6} cm^3 (STP)/cm^2.s.cmHg). Selectivity (a dimensionless parameter) of asymmetric membrane can be determined by

$$\alpha_{ji} = P_i/P_j = (P/l)_i / (P/l)_j$$

Scanning electron microscope

The fibers were cut to the lengths of 1-2 mm using a fresh razor blade and were snapped under liquid nitrogen, which gives a generally clean break. The fibers were then mounted on sample stubs. These samples were then sputtered with gold before a surface scanning investi-

Table 1. General spinning conditions

Spinning dope compostion	26.0 wt. % of polysulfone, 30.4 wt. %of N, N-dimethylacetamide 30.4 wt. % of Tetrahydrofuran 13.2 wt. % Ethanol
Spinning dope temperature	Ambient temperature (27°C)
Spinneret dimensions	OD 600 μm/ID 290 μm
Internal coagulant composition	20.0 wt. % potassium acetate in water
Internal coagulant temperature	Ambient temperature (27°C)
Dope extrusion rate: Internal coagulant injection rate	3:1
Forced convection gas	Nitrogen
Forced convection flow rate	4 l/min
External bath composition	Tap Water
External bath temperature	14°C
Jet stretch ratio	1

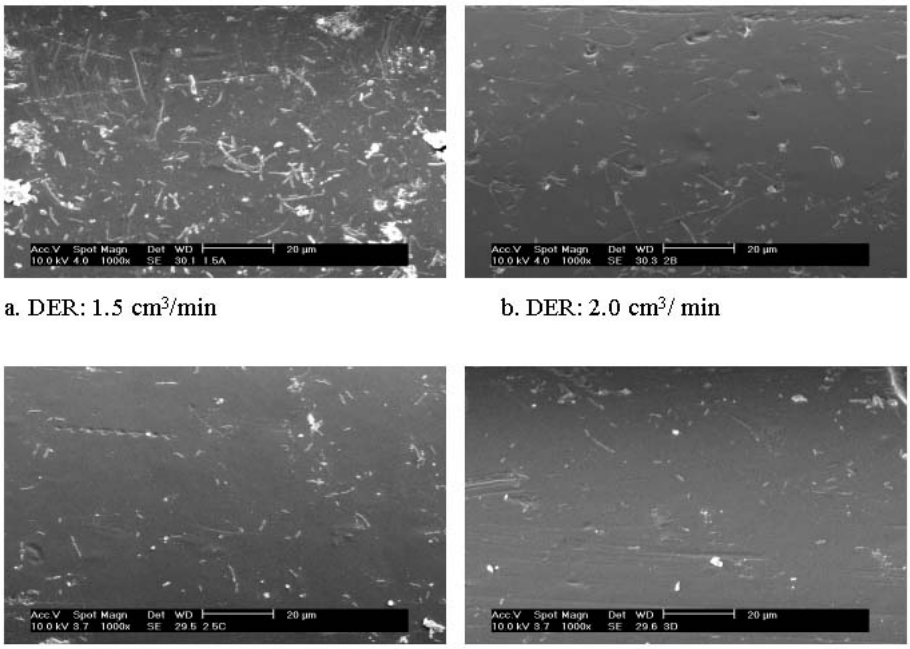
gation using an SEM (SEMEDAX; XL40; PW6822/10).

Results and Discussion

Effect of dope extrusion rate on the morphology of asymmetric polysulfone hollow fiber membrane

The SEM imaging of the outer surface and partial cross section of hollow fibers spun with different dope extrusion rates are shown in Figures 1-3. Figures 1 and 2 illustrate the SEM pictures of the outer surface of uncoated and coated hollow fibers, respectively. There were apparent differences for these fibers at this magnification. Figure 1 shows that imperfections prevail while in Figure 2 no imperfections can be observed. Therefore, membranes in Figure 1 were not practically useful and coating was needed to heal the surface imperfections (Henis *et al*., 1981). Since tap water was chosen as the external coagulant, the resultant fibers had a relatively dense outer layer regardless of low or high dope extrusion rates. This is because an outer skin was formed on top of an open-cell porous substructure caused by instantaneous liquid-liquid demixing process (Wijmans *et al*., 1983). Figure 3 shows the pictures of the partial cross section of hollow fibers. As the dope extrusion rate increases, there is a transformation from thick skin and few circular macrovoids to thin skin and many teardrops or finger macrovoids.

Although a constant ratio of dope extrusion rate to bore fluid flow rate was employed in order to maintain a similar solvent exchange rate, the outer diameter and inner diameter were slightly increased with the increase of dope extrusion rate. This is believed to be due to the rate of skin formation and solidification being a function of mass transfer rate during solvent exchange. As the dope extrusion rate is increased, the spinning speed increases and the mass transfer between the outer skin of the moving nascent fiber and water are significantly enhanced. As a result, the



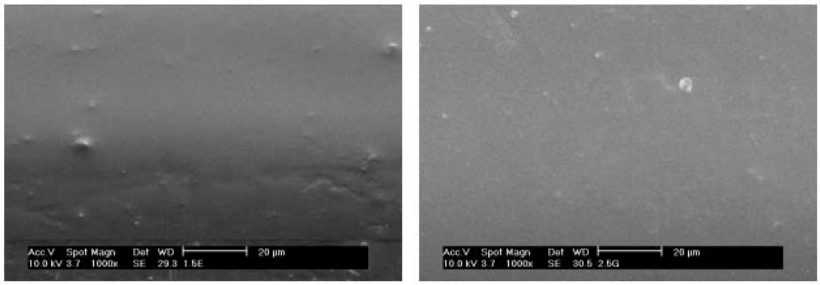
a. DER: 1.5 cm^3/min

b. DER: 2.0 cm^3/ min

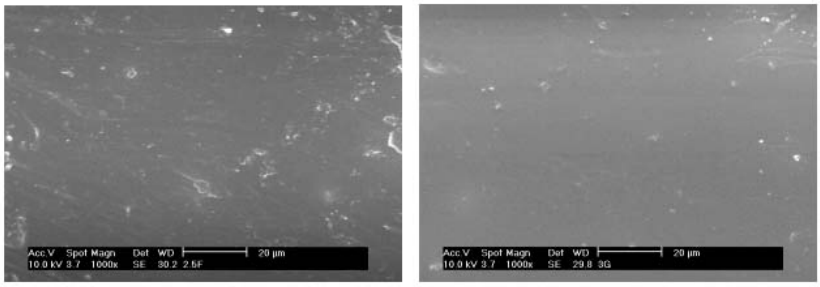
c. DER: 2.5 cm^3/min

d. DER: 3.0 cm^3/ min

Figure 1. The uncoated outer surface of hollow fibers spun at various dope extrusion rates (magnification × 1000)

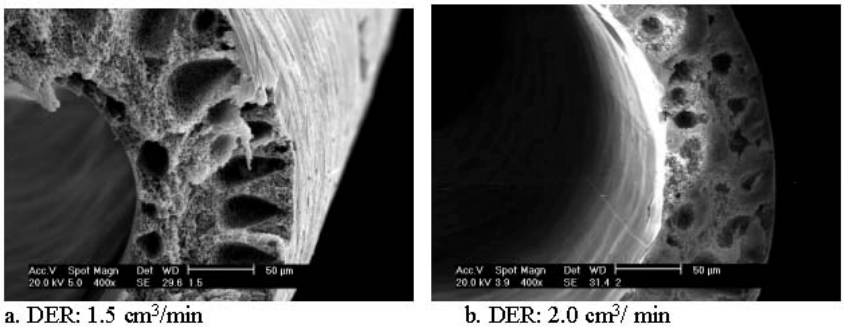


a. DER: 1.5 cm^3/min b. DER: 2.0 cm^3/ min

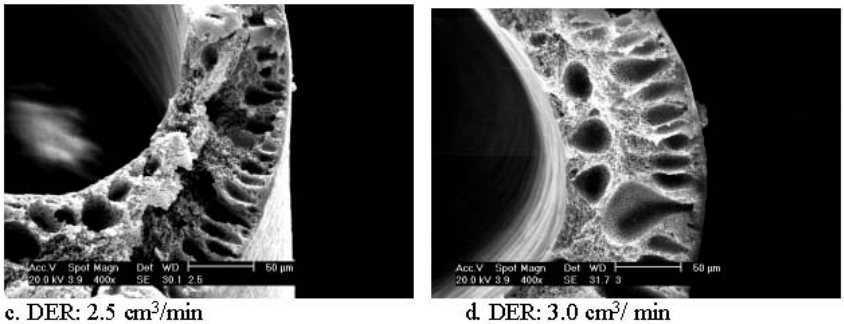


c. DER: 2.5 cm^3/min d. DER: 3.0 cm^3/ min

Figure 2. The coated outer surface of hollow fibers spun at various dope extrusion rates (magnification × 1000)



a. DER: 1.5 cm^3/min b. DER: 2.0 cm^3/ min



c. DER: 2.5 cm^3/min d. DER: 3.0 cm^3/ min

Figure 3. The partial cross section of hollow fibers spun at various dope extrusion rates (magnification × 400)

outer and inner fiber diameters were increased with increasing dope extrusion rate (Chung *et al*., 2000). The dimensions of the hollow fibers spun with different dope extrusion rates are presented in Table 2.

Ekiner and Vassilatos (1990) recommended that a value of 2 for the outer diameter to inner diameter ratio should be maintained to give a very good separation performance. In this study the ratio of the outer diameter to inner diameter was found to be in the range of 1.9-2.0.

Effect of dope extrusion rate on the gas separation performance of asymmetric polysulfone hollow fiber membrane

According to the experimental data shown in Table 3, Figure 4 and Figure 5, it can be clearly observed that pressure-normalized flux and selectivity for the uncoated and coated hollow fiber membranes were increased with the increasing dope extrusion rates. When DER is increased, it is believed that the molecular orientation in the fiber skin was enhanced, which in turn boosted membrane pressure-normalized flux and selectivity (Ismail *et al*., 1999).

This contradicts the results achieved by Chung *et al*. (2000). In their study, it was found that, in low shear rate regions, the decrease in pressure-normalized flux or increase in selectivity with increasing shear rates occurred from better molecular orientation and chain packing induced by shear. In high shear regions, the increase in pressure-normalized flux or decrease in selectivity was mainly attributed to relatively porous skin structures.

Hence, the selection of bore fluid plays an important role in controlling the pressure-normalized flux and selectivity of the membrane with the increasing of dope extrusion rates. According to Pesek and Koros (1994), Ismail (1997) and Sharpe *et al*. (1999), bore fluid with lower water activity tends to give higher selectivity for polysulfone gas membranes. Using these low water activity bore fluids was believed to slow down the solvent migration into the bore and prevented the active layer from perforation. Pesek and Koros (1994) also believed that lower water activity of bore fluid allowed better control of the two phase

Table 2. Dimensions of the hollow fibers spun with different dope extrusion rates

DERs cm^3/min	Shear rates s^{-1}	OD μm	ID μm	Wall thickness μm	OD:ID μm
1.5	463.34	508	259	249	1.9
2.0	608.02	516	263	253	1.9
2.5	696.69	551	275	276	2.0
3.0	842.13	560	286	274	1.9

Table 3. Pressure-normalized flux and selectivity of uncoated and coated hollow fiber membrane spun with different dope extrusion rate.

DERs	Shear rates	Uncoated GPU		Coated GPU	
cm^3/min	s^{-1}	P_{O_2}	α_{O_2/N_2}	P_{O_2}	α_{O_2/N_2}
1.5	463.34	6.53	1.11±0.05	1.74	3.89±0.19
2.0	608.02	11.34	1.58±0.05	2.81	4.32±0.05
2.5	696.69	19.41	1.87±0.07	3.41	4.48±0.07
3.0	842.13	11.60	0.87±0.02	2.32	2.52±0.05

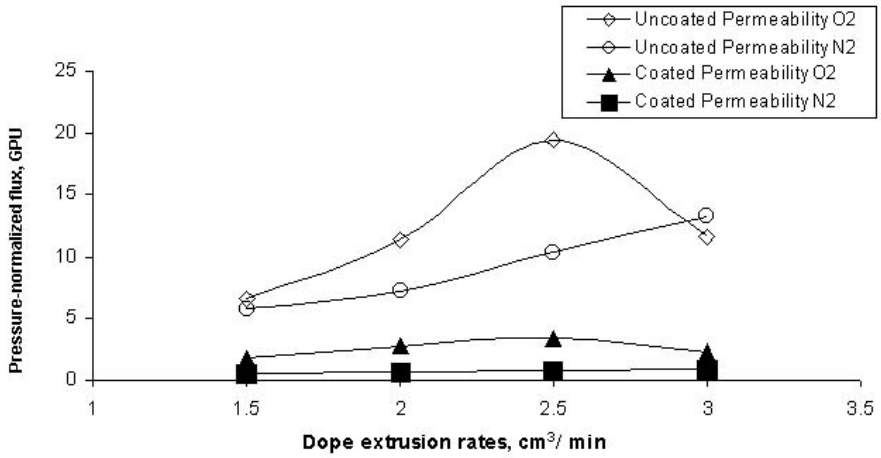


Figure 4. Effect of dope extrusion rates on pressure-normalized flux of uncoated and coated hollow fiber membrane spun at different dope extrusion rates

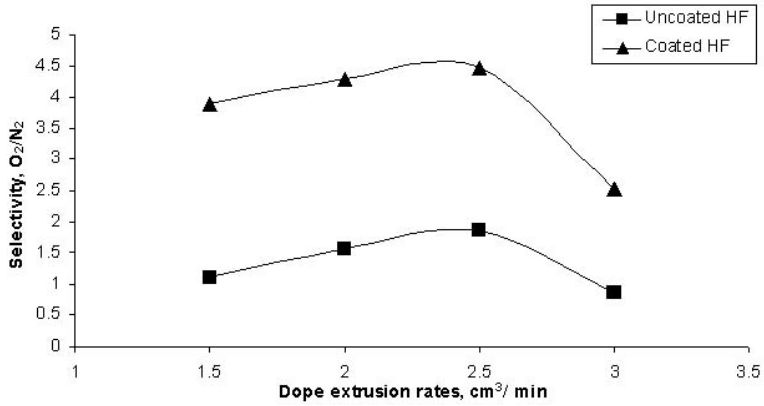


Figure 5. Effect of dope extrusion rates on selectivity of uncoated and coated hollow fiber membrane spun at different dope extrusion rates

separation processes occurring simultaneously at the internal and external surfaces of their polysulfone hollow fiber membrane. Ismail (1999) stated that the combination of a high extrusion rate and less water activity of the bore fluid produced highly selective polysulfone hollow fiber membranes. The highly engineered active layer produced can deliver selectivities beyond those predicted by the solution diffusion mechanism.

Figure 4 and Figure 5 clearly show that the critical dope extrusion rates (shear rates) for the uncoated and coated hollow fiber membranes were determined to be around 2.5 cm^3 /min. According to this critical point, Ismail *et al*. (1997) and Shilton *et al*. (1994 and 1997) stated that increasing the dope extrusion rates enhanced molecular orientation and free volume in skin layer, hence improving pressure-normalized flux and selectivity of the membrane itself.

At an extremely high dope extrusion rates (shear rate) that is over its critical point, an abrupt reduction in selectivity was observed. There was a decrease in pressure-normalized flux of oxygen for both uncoated and coated hollow fiber membranes. Although increasing the shear induces the molecular orientation, it also causes a reduc-

tion in skin thickness and strength, which eventually results in surface defects that undermine the enhancement in selectivity (Sharpe *et al*., 1999).

Conclusion

Increasing dope extrusion rates have a significant effect on the morphology and gas separation performance of asymmetric hollow fiber membranes. In this study, it has shown that pressure-normalized flux and selectivity were increased by increasing dope extrusion rates (shear rates) and lowering water activity in bore fluid. This is due to the reduction in skin thickness and enhanced molecular orientation in the skin layer. The critical dope extrusion rates (shear rates) for the uncoated and coated hollow fiber membrane were determined to be around 2.5 cm^3/min.

Nomenclature

A	Membrane effective area
L	Membrane thickness or skin layer thickness
Δp	Pressure difference
P	Permeability coefficient
P/l	Pressure-normalized flux or permeability
Q	Volumetric flow rate
α	Selectivity
I	Component i
J	Component j

References

Aptel, P., Abidine, N., Ivaldi, F., Lafaille, J.P. 1985. Polysulfone hollow fibers - effect of spinning conditions on ultrafiltration properties. J. Membr. Sci., 22:199-215.

Chung, T.S., Lin, W.H., Vora, R.H. 2000. The effect of shear rate on gas separation performance of 6 FDA-durene polymide hollow fibers. J. Membr. Sci., 167:55-66.

Chung, T.S., Qin, J.J., Gu, J. 2000. Effect of shear rate within the spinneret on morphology, separation performance and mechanical properties of ultrafiltration polyehtersulfone hollow fiber membranes. Chemical Engineering Science., 55: 1077-1091.

Chung, T.S., Teoh, S.K., Hu, X. 1998. Formation of ultrathin high-performance polyethersulfone hollow fiber membranes. J. Membr. Sci., 133: 161-175.

East, G.C., McIntyre, J.E., Rogers, V. and Senn, S.C. 1986. Production of Porous Hollow Polysulfone Fibers For Gas Separation. **In** Proceeding of the Fourth BOC Priestly Conference. Royal Society of Chemistry. London (Special Publication No.62): 16-18.

Ekiner, O.M. and Vassilatos, G. 1990. Polyamide hollow fiber for hydrogen/methane separation-spinning and properties. J. Membr. Sci., 53: 259-273.

Hachisuka, H., Ohara, T., and Ikeda, K. 1996. New type asymmetric membranes having almost defect free hyper-thin skin layer and sponge-like porous matrix, J. Membr. Sci. 116: 265-272.

Henis, J.M.S. and Tripodi, M.K. 1981. Composite hollow fiber membranes for Gas separation: The resistance model approach. J. Membr. Sci., 8: 287-299.

Henmi, M., Yoshioka. T. 1993. Hollow fiber membrane based on polyacrylonitrile with a high degree of polymerization and its properties. J. Membr. Sci., 85: 129-138.

Ismail, A.F. 1997. Novel Studies of Molecular Orientation in Synthetic Polymeric Membranes for Gas Separation. University of Strathclyde, Glasgow: PhD Thesis.

Ismail, A.F., Dunkin, I.R., Gallivan, S.L. and Shilton, S.J. 1999. Production of super selective polysulfone hollow fiber membranes for gas separation. Polymer., 40. 6499-6506.

Ismail, A.F., Shilton, S.J., Dunkin I.R. and Gallivan, S.L. 1997. Direct measurement of rheologically induced molecular orientation in gas separation hollow fiber membranes and effects on selectivity. J. Membr. Sci., 126: 133-137.

Koros, W.J. and Fleming, G.K. 1993. Membrane-based gas separation. J. Membr. Sci., 83: 1-80.

McKelvey, S.A., Clausi, D.T., Koros, W.J. 1997. A guide to establishing hollow fiber macroscopic properties for membrane applications, J. Membr. Sci., 124: 223-232.

Pesek, S.C. and Koros, W.J. 1994. Aqueous quenched asymmetric polysulfone hollow fibers prepared by dry/wet phase separation. J. Membr. Sci., 88: 1-19.

Pinnau, I., Wijmans, J.G., Blume, I., Kuroda, T., Peinemann, K.V. 1988. Gas permeation through composite membranes. J. Membr. Sci., 37: 81-88.

Puri, P.S. 1990. Fabrication of hollow fibre gas separation membranes. Gas Separation and Purification., 4: 29-36.

Sharpe, I.D., Ismail, A.F. and Shilton, S.J. 1999. A study of extrusion shear and forced convection residence time in the spinning of polysulfone hollow fiber membranes for gas separation. Separation and purification technology., 17: 101-109.

Shilton, S.J., Bell, G. and Ferguson, J. 1994. The rheology of fiber spinning and the properties of hollow-fiber membranes for gas separation. Polymer., 35: 5327-5335.

Shilton, S.J., Bell, G. and Ferguson, J. 1996. The deduction of fine structural details of gas separation hollow fiber membranes using resistance modelling of gas permeation. Polymer., 37: 485-492.

Shilton, S.J., Ismail, A.F., Gough, P.J., Dunkin, I.R. and Gallivan, S.L. 1997. Molecular orientation and the performance of synthetic polymeric membranes for gas separation. Polymer., 38: 2215-2220.

Torrestiana-Sanchez, B., Ortiz-Basurto, R.I. and Brito-De La Fuente, E. 1999. Effect of non-solvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes, J. Membr. Sci., 152: 19-28.

van't Hof, J.A., Reuvers, A.J., Boom, R.M., Rolevink, H.H.M., Smolders, C.A. 1992. Preparation of asymmetric gas separation membranes with high selectivity by a dual-bath coagulation method, J. Membr. Sci., 70: 17-30.

Wijmans, J.G., Baaij, J.P.B. and Smolders, C.A. 1983. The mechanisms of microporous or skinned membranes produced by immersion precipitation. J. Membr. Sci., 14: 263-274.

Yean, L.P. 2002. Development of defect-free and ultra thin-skinned asymmetric membranes for gas separation. Department of Chemical Engineering, Universiti Teknologi Malaysia: MSc. Thesis