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EFFECTS OF FABRICATION PARAMETERS ON THE MORPHOLOGY OF POROUS POLYSULFONE HOLLOW FIBER MEMBRANES

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Abstract. Porous Polysulfone (PSf) hollow fiber membranes with high porosity were fabricated via a wet spinning phase inversion method, using N-methyl-1-pyrrolidone (NMP, >99.5%) as solvent, Glycerol as pore-forming additive and water as the coagulation medium. With the addition of the Glycerol, the effect of external coagulation bath composition, dope extrusion rate, additive concentration and post treatment with pure ethanol on the structure of membranes was investigated. The gas permeation method was used to estimate the mean pore size and effective surface porosity of the PSf hollow fiber membranes prepared. The hydrophobicity of the hollow fiber membranes was characterized in terms of contact angle and wetting pressure. Also, mechanical strength of the hollow fibers was tested by collapsing pressure. The fabricated membranes are applicable for membrane gas absorption processes.

Keywords: Membrane characterization; polysulfone; porous hollow fiber membrane

Abstrak. Membran gentian gelonggang berliang polysulfon (PSf) dengan keliangan yang tinggi telah dihasilkan melalui kaedah pemintalan fasa songsang basah, menggunakan N-methyl-1-pyrolidone (NMP, >99.5%) sebagai pelarut, glycerol sebagai penambah penghasilan liang dan air sebagai komposisi media pengentalan, kadar penyemperitan dop, kepekatan penambah dan rawatan selepas dengan ethanol tulen ke atas struktur memmbran telah dikaji. Kaedah penelapan gas telah digunakan untuk menganggarkan purata saiz liang dan keliangan permukaan efektif untuk membran gentian gelonggang polysulfon (PSf) yang dihasilkan. Kadar hidroforbik membran gentian gelonggang telah dicirikan melalui sudut sentuhan dan tekanan pembasahan. Juga kekuatan mekanikal membran gentian gelonggang telah diuji dengan kejatuhan tekanan. Membran yang dihasilkan adalah sesuai untuk digunakan dalam proses-proses penyerapan gas.

Kata kunci: Pencirian membran; polysulfon; membran gentian gelonggang berliang

1.0 INTRODUCTION

Applications of porous membranes have attracted considerable attention, particularly in the area of membrane-based gas absorption (Li *et al.,* 1998; Feron and Jensen, 2002; Dindore *et al.,* 2004; Wang *et al.,* 2005; Bottino *et al.,* 2008; Park *et al.,* 2008) where the high hydrophobicity, low membrane transport resistance, and excellent

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chemical resistance to various chemical-feed streams are the essential properties of these membranes. Membranes with low resistance could be obtained by increasing the membrane surface porosity and reducing the thickness of the membrane separation layer. Also for the membrane hydrophobicity, despite depending on the property of the membrane material, it could also be adjusted by the membrane pore size, as suggested by the Laplace-Young equation (Kim and Harriott, 1987).

In fact, hydrophobic porous hollow fiber membranes with high porosity can be formed by a simple and convenient method of non-solvent induced phase inversion separation (NIPS) process, if a suitable solvent can be found for the selected polymer. Membrane structure and morphology can also be optimized by adjusting various fabrication parameters. However, only a limited studies has been made on the preparation of membranes for gas absorption applications (Li *et al.,* 1999; Ren *et al.,* 2006; Atchariyawut *et al.,* 2006). Atchariyawut *et al.*, 2006 fabricated PVDF microporous hollow fiber membranes using different dope solutions containing NMP and different additives (phosphorous acid and glycerol). The resultant hollow fibers with different structures were used to make membrane modules, which were applied as gas-liquid membrane contactors for CO_2 absorption in water.

Polysulfone (PSf) has been widely used as a membrane material due to its hydrophobicity, mechanical strength, thermo-stability and stability against chemicals. PSf is also an excellent material for the preparation of hollow fiber membranes. In addition, the above properties of this polymer provide a potential application in the membrane gas absorption processes. Thus, we attempted to prepare several porous PSf hollow fiber membranes with high surface porosity (high permeability), small pore size and ultra-thin skin layer via phase inversion method. The main purpose of this work is to investigate the effect of some spinning parameters such as dope extrusion rate, additive concentration, external coagulation bath composition and post treatment on the morphology and structure of the PSf hollow fiber membranes for using as membrane gas absorption. Then fabricated membranes will be characterized by gas permeation method, wetting pressure, collapsing pressure and contact angle.

2.0 EXPERIMENTAL

2.1 Materials

PSf (Udel P-3700) was supplied by Solvay Advance Polymers. The polymer was dried at 60 °C for 10 h. *N*-methyl-1-pyrrolidone (NMP >99.5%), was supplied by MERCK and used as solvent without further purification. Glycerol (anhydrous extra pure) was purchased from MERCK (Germany) and used as non-solvent additive in the polymer solution. A mixture of 70% distilled water and 30% NMP was used as internal coagulant in order to remove inside skin layer. Tap water was used as the external coagulant and washing medium. And also, mixtures of 10, 30 and 50 wt.%

of Ethanol with tap water were tested as external coagulant. Pure Ethanol (99.8% MERCK) was used for post treatment of the hollow fibers.

2.2 Fabrication of Polysulfone Hollow Fiber Membranes

The PSf polymer (pellet form) was dried at 60±2 °C in a vacuum oven for 12 h to remove moisture content. The spinning dope solution of 22 wt% PSf and 88% NMP was prepared (at the room temperature 25 – 27 °C) by stirring until the solution became homogeneous. The addition of Glycerol (5, 7 wt.%) as a non-solvent has two functions: not only can it result in a rapid phase separation and obtain a thin skin layer; it also behaves as a pore facilitating agent to produce membranes with porous structure.

The hollow fiber spinning process by the dry-jet wet phase inversion was explained elsewhere (Ismail *et al.,* 1999). The dope solutions were degassed before spinning. The bore fluid was fed into the inner tube of spinneret and dope solutions were fed into the annulus of the spinneret separately by a gear pump. Table 1 lists the detailed spinning parameters. Tap water and Mixture of tap water/Ethanol were used as the external coagulant to solidify the PSf polymer solution to form hollow fiber membranes. The spun fibers were immersed in water for 3 days to remove the residual NMP and Glycerol. Some fibers were post-treated by the ethanol as solvent exchange. The hollow fibers was immersed in ethanol for 30 min. in order to replace water and gradually reduce the effect of surface tension during drying to minimize fiber deformation and pore collapse before drying at room temperature.

Table 1 Spinning condition of fabricating PSf hollow fiber membranes

Dope solution flow rate (ml/min)	2.8 - 4.5
Bore fluid composition (wt%)	NMP/H_2O 30:70
Bore fluid flow rate (ml/min)	3.00
External coagulant	tap water and EtOH/water
Air gap distance (cm)	0.0
Spinneret od/id (mm)	1.20/0.51
Coagulation temperature °C	25
Room relative humidity (%)	70 - 75

2.3 Gas Permeation Method

For a porous asymmetric membrane, the determination of pore size, particularly surface porosity over effective pore length, is very important in studying mass transfer in the membrane absorption. However, the gas permeation method suggested by Yasuda and Tsai, 1974 was useful in determining the volume porosity of porous

membranes; Li *et al.*, 1999 introduced a modified gas permeation method to determine the mean pore size and the effective surface porosity over the effective pore length of the asymmetric membrane. As indicated by Shih *et al.*, 1990, although the magnitude of mean pore size, does not have any significant physical meaning, especially for the membranes prepared by phase inversion processes, it represent a parameter which can be compared quantitatively for the membranes prepared under different spinning conditions. For a considerable porous asymmetric membrane, the total gas permeation rate through the asymmetric membrane is the combination of Poiseuille flow and Knudsen flow (Wang *et al.,* 1995).

If we assume that the pores in the skin layer are approximated by cylindrical pores with the modal pore radius, r, and the effective length, L_p, Eq. (1) can be obtained (Li *et al.,* 1999):

$$J_i = 0.666\left(8RT/\pi M\right)^{0.5}\left(r\varepsilon/RTL_p\right)+\left(\overline{P}r^2\varepsilon/8\mu_i RTL_p\right) \quad \text{or} \quad J_i = P_{0\overline{P}} + K_0 \quad (1)$$

By plotting J_i with mean pressures according to Eq. (1), the mean pore size can be calculated from the intercept (K_0) and slope (P_0):

$$r = 5.333\left(P_0/K_0\right)\left(8RT/\pi M\right)^{0.5}\mu \quad (2)$$

The effective surface porosity over pore length, ε/L_p can also obtain from the slope as follows:

$$\varepsilon/L_p = 8\mu RTP_0/r^2 \quad (3)$$

Pure N_2 was used as the test gas. The test apparatus used was based on the volume displacement method. The upstream pressure was in the range from 0.5 to 4 bar (gauge). The N_2 permeation rate was measured at 25 °C in atmosphere using soap-bubble flow meter. The gas permeability was then calculated according to outer diameter of the hollow fiber.

2.4 Wetting Pressure, Collapsing Pressure and Contact Angle

The test module was used to determine the collapsing pressure and wetting pressure. In testing wetting pressure, distilled water was fed into the shell side in the module. The pressure slowly increased by a pump at 0.5 bar interval. At each pressure interval, the membrane module was kept at the constant pressure for 30 min. to check if any water has permeated into the fiber tube side. By increasing pressure in the shell side, when a continuous flow is observed in the tube side it is a sign of collapsing the hollow fiber. And also, contact angle of the dried hollow fibers with water was measured by the sessile drop technique using a goniometer (model G1**,** Krüss GmbH**,** Hamburg**,** Germany).

The resulting PSf hollow fiber membranes properties are given in Table 2.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Dope Extrusion Rate

It was demonstrated that increase in dope extrusion rate DER will enhance molecular orientation of polymer in the skin layer of the hollow fibers which will increase membrane selectivity (Ismail *et al.,* 1997). It can be seen from Figure1 that pressure normalized flux of prepared membranes decrease considerably with an increase in the DER. It can attribute to formation of outer dense skin layer where the inner skin layer almost removed by reducing water activity in the bore side in wet spinning process.

The data in Table 2 show that as the DER increases, pore diameter increase results in significant decrease of surface porosity. It shows that formation of dense skin layer can reduce amount of open end pores and make pores bigger. The dense skin layer can improve mechanical strength of the membrane in term of collapsing pressure. The hydrophobicity of the membrane was also found to increase with DER as the contact angle and wetting pressure data show in Table 2.

Table 2 Hollow fiber spinning solution, coagulation bath composition, dope extrusion rate, wetting pressure, collapsing pressure, pore diameter, surface porosity and contact angle

Membrane No.	Glycerol wt%	dope extrusion rate DER (ml/min.)	coagulation bath comp. EtOH Wt%	pore diameter (μm)	surface porosity ε/L_p (10^{-2} m^{-1})	wetting pressure (bar)	collapsing pressure (bar)	contact angle (θ)
M1	0	2.8	0	0.0035	558	8	10	78
M2	0	3.5	0	0.004	258	8	10.5	83
M3	0	4.2	0	0.0043	232	8.5	12	85
M4	0	4.5	0	0.0057	87.2	10.5	13	85
M5	0	4.2	10	0.0043	232	11.5	14	86
M6	0	4.2	30	0.0047	314	9.5	13.5	79
M7	0	4.2	50	0.0057	872	8	10	75
M8	5	4.5	0	0.003	141	13	15	84
M9	7	4.5	0	0.0035	121	11.5	14	86
post treated	0	4.5	0	0.0066	224	12	15	85

3.2 Effect of Glycerol Concentration

It has been reported that the properties of polymer membranes could be improved by introducing non-solvent additives in the polymer solution. Generally, high porous membranes with well-interconnected pores and surface properties can be produced by using a suitable non-solvent additive (pore former) such as water, glycerol, polyethylene glycol (PEG), lithium chloride (LiCl), phosphoric acid, ethanol, or

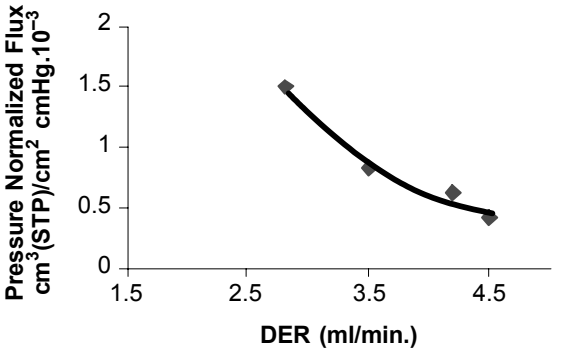

Figure 1 Effect of dope extrusion rate on pressure normalized flux (pure nitrogen at 1 bar) of the hollow fiber membranes.

polyvinylpyrrolidone (PVP) (Han and Nam, 2002; Wang *et al.,* 2000; Xu and Qusay, 2004).

The gas permeation data for M4, M8 and M9 membranes in Table 2 show that an increase in Glycerol concentration in dope solution until 5 wt% results in smaller pore diameter and higher surface porosity. By increasing Glycerol more than 5 wt% the opposite trend is observed. Therefore, it can be concluded that non-solvent additive into dope solution can enhance phase inversion rate results in smaller pore diameter and higher surface porosity. And if the additive reaches to more than certain amount (rapid phase inversion) tend to form macro-voids in the structure of membrane results in bigger pores and lower surface porosity (Kesting, 1991). Finally, the addition of Glycerol in the polymer dope shows a slight decrease in the mean pore size, but a drastic increase in the effective surface porosity as compared to that without addition of Glycerol.

Bigger pores tend to lower wetting pressure and there is also no considerable change on the contact angle (see Table 2). So, it reveals that Glycerol can not make a slight change on the surface morphology of the membrane.

3.3 Effect of External Coagulation Bath Composition

External coagulation bath plays an important role in the formation of membranes by phase inversion processes. In general, the fast coagulation rate results in a formation of large finger-like macro-voids structures, whereas the slow coagulation rate results in a porous sponge-like structure (Kesting, 1991). The presence of Ethanol in the coagulation bath was believed to reduce the polymer precipitation rate in phase inversion process. The slow precipitation could be explained on the basis of inter-diffusion of NMP, Ethanol and water system. This is because the solvent-nonsolvent interactions based on the solubility parameters (Deshmukh and Li, 1998).

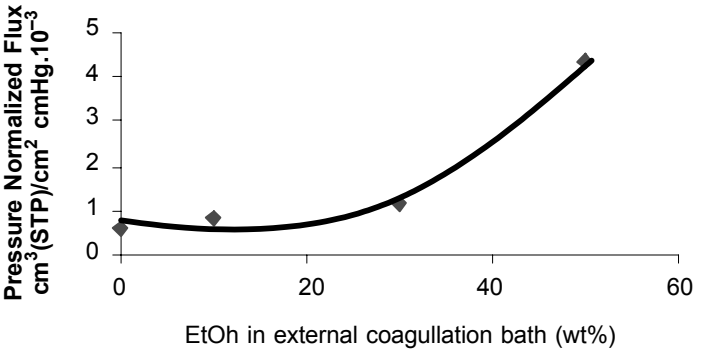

Figure 2 Effect of coagulation bath composition on pressure normalized flux

The gas permeation results of M3, M5, M6 and M7 membranes in Table 2 reveal that, the effective surface porosity (open-end pores) and pore diameter increase as ethanol concentration in the coagulation bath is increased. As mentioned before, an increase in the Ethanol content in the external coagulation bath results in a decrease in the precipitation rate, which leads to a change in the membrane surface morphology.

As, it can be seen in Figure 2 pressure normalized flux of prepared membranes also increase gradually with Ethanol concentration in coagulation bath until 30 wt% after it increase sharply.

It means that at higher ethanol concentration (more than 30 wt%) outer skin layer seem to remove and results in membranes with high pressure normalized flux and low collapsing pressure.

Therefore, as the data in Table 2 shows an increase in coagulation bath concentration can change hydrophobicity of the membrane results in reducing contact angle and wetting pressure.

3.4 Effect of Post Treatment

Shrinkage of the wet PSf hollow fiber during the drying process would reduce the porosity and pore size. In order to reduce the shrinkage, the organic non-solvent exchange method was used to treat the wetted membranes. In this process, water in the membrane pores was replaced by the low surface tension alcohol. The selected hollow fibers (M4) immersed in pure Ethanol for 30 min. then dried at the ambient condition for 3 days. The structure parameters determined are shown in Table 2. The mean pore and effective surface porosity of the result membrane were increased significantly, although the hydrophobicity of the membrane in term of contact angle and wetting pressure remained constant. The pressure normalized flux of treated membrane was found 2-3 fold more than non-treated membranes

(1.19×10^{-3} cm^3/cm^2.s.cmHg). The most possible reason was that a post treatment of the membranes with a low-surface tension non-solvent, such as Ethanol, may help to prevent collapse and closure of pores when the non-solvent evaporated into the atmosphere during drying of the fibers in the air.

4.0 CONCLUSION

In order to fabricate membranes with high surface porosity (high permeability), higher hydrophobicity and mechanical strength which is appropriate for membrane gas absorption, PSf hollow fiber membranes were prepared from 22% Udel P-3700 in NMP by a wet spinning technique. Effects of dope extrusion rate, external coagulation bath composition, Glycerol concentration as a pore- forming additive in the polymer dope and post treatment on the morphology of PSf membranes were studied using the gas permeation method. The hydrophobicity of membranes was determined in terms of wetting pressure and contact angle and also mechanical strength of the hollow fiber membranes was examined in term of collapsing pressure.

The results from the gas permeation method indicate that membranes with high surface porosity can be fabricated at lower DER and sufficient amount of Glycerol (5 wt%) as additive. Also, external coagulation bath composition increased the surface porosity significantly.

Although, hydrophobicity and mechanical strength of the membranes were increased at higher DER, Increasing Ethanol in external bath showed adverse effect. The post treated membranes showed good surface porosity and hydrophobicity.

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NOTATION

J gas permeation flux (mol.m^{-2} Pa^{-1} s^{-1})
L_p effective pore length (m)
M molecular weight of the gas
$\overline{P}$ mean pressure (Pa)
R gas constant (8.3144 m^3 Pa mol^{-1} K^{-1})
r mean pore radius of the membrane (m)
ε porosity
μ dynamic viscosity (Pa.s)

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