

Preparation of PVDF Hollow-Fiber Membranes via Immersion Precipitation

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ABSTRACT: Porous polyvinylidene fluoride (PVDF) hollow-fiber membranes with high porosity were fabricated using the immersion precipitation method. Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were used as solvent, respectively. In addition, polyvinylpyrrolidone (PVP), lithium chloride, and organic acids were employed as nonsolvent additives. The effects of the internal and external coagulation mediums on the resulting membrane properties were also investigated. The resulting hollow-fiber membranes were characterized in terms of maximum pore radius, mean pore radius, effective surface porosity as well as wetting pressure. The structures of the prepared hollow fibers were examined using a scanning electron microscope. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1643–1653, 2001

Key words: polyvinylidene fluoride; hollow-fiber membrane; nonsolvent additive

INTRODUCTION

Applications of porous membranes have attracted considerable interest, particularly in the areas of membrane-based gas absorption or stripping, oil/water separation, and membrane distillation^{1–7} where the high hydrophobicity, low membrane transport resistance, and excellent 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 porosity and reducing the thickness of the membrane separation layer. As 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 equation.

In the above-mentioned applications, polytetrafluoroethylene (PTFE), polypropylene (PP) and polyvinylidene fluoride (PVDF) are among the popular hydrophobic materials. To date, commercially available polytetrafluoroethylene (PTFE) flat sheet or tubular membranes and polypropylene (PP) hollow-fiber membranes, produced by stretching or thermal method,^{8,9} are being widely employed in these processes. Although these membranes show excellent hydrophobicity, high membrane resistance, however, is inevitable due to their symmetric structures of membrane morphology produced via the above methods. Furthermore, polypropylene membranes cannot withstand high pH (pH > 9) and high concentration of free chloride.

Polyvinylidene fluoride (PVDF), on the other hand, offers many advantages as a separation membrane material. As a semicrystalline polymer containing crystalline and amorphous and/or rubbery phase, its crystalline phase provides

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thermal stability while the latter provides the desired membrane flexibility. Also, credits should be directed to its high hydrophobicity as well as excellent chemical stability against corrosive chemicals and organic compounds including acids, alkaline, strong oxidants, and halogens.^{10,11} In addition, its ease of fabrication into asymmetric hollow-fiber membranes with low mass transfer resistance via the dry-wet phase inversion method is nevertheless another attractive feature. These advantages, along with good physical and thermal stability, enable this polymer material to have outreached its competitors.

Numerous literatures related to the preparation, morphology, and performance of flat sheet PVDF membranes have been reported by quite a number of researchers in the past.¹²⁻²² In general, these literatures emphasized greatly on the casting of flat-sheet membranes from binary solutions consisting of PVDF with a strong polar high boiling point solvent such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP); or from ternary solutions containing another low boiling point solvent such as acetone and tetrahydrofuran (THF) or a suitable nonsolvent additive (pore former) such as glycerol, polyethylene glycol (PEG), lithium chloride (LiCl), phosphoric acid, ethanol, or polyvinylpyrrolidone (PVP). Among others, the concentration of polymer solution is one of the factors affecting the membrane performance.

Contrary to numerous works done on flat-sheet PVDF membranes, only a few studies have been reported and patented on the preparation of PVDF asymmetric hollow-fiber membranes.²³⁻²⁵ Comprehensive research on the development of asymmetric PVDF hollow-fiber membranes with good performance (i.e., high-permeation flux and hydrophobicity) is still lacking.

In practice, conditions favoring the preparation of high-performance flat-sheet membrane could provide some insights to the development of hollow-fiber membranes. The actual formation conditions of hollow fiber, however, differ considerably from that of flat-sheet membranes. Therefore, the conditions similar to those used in the formation of flat-sheet membranes cannot be simply extended to produce hollow-fiber membranes. An essential difference in the dope formulation of flat-sheet and hollow-fiber membranes is their dope viscosity required to cast or spin. Generally, a flat-sheet membrane can be cast from a polymer dope with its viscosity as low as a few hundred

centipoises, while a minimum dope viscosity required to spin hollow fibers is of the order of a few thousand centipoise.²⁶ For flat-sheet membranes, the phase inversion process starts from the top surface of a cast film, whereas for hollow-fiber membranes via dry-wet spinning, the phase inversion process starts immediately after extrusion from a spinneret at the inner surface of the hollow fiber by the internal coagulant and then at the outer surface of the hollow fiber upon immersion in an external coagulation bath, or when a wet spinning method is used, the phase inversion process begins at both the inner and outer surface at the same time.

Among many factors affecting the characteristics, morphology, and properties of the resulting hollow fibers, namely polymer concentration, solvent/nonsolvent system, additives in the dope solution, compositions of internal and external coagulants, spinning parameters such as extrusion rate, take-up velocity, and air gap, have been explained in great detail²⁷⁻³¹ and, thus, it is needless to repeat here.

Because polyvinylidene fluoride (PVDF) has a critical surface tension of about 25 dynes/cm, the coagulation rate and fibers solidification must be slow due to the weak interaction between the nonsolvent (i.e., water) and the polymer during the fabrication process. Therefore, considerable difficulties would be expected in the spinning of porous asymmetric PVDF hollow-fiber membranes via the dry-wet phase inversion method. Therefore, addition of water-soluble nonsolvent additives in the spinning solution would be a good way to increase the precipitation rate of the polymer solution.

This study aimed to prepare asymmetric porous PVDF hollow fiber membranes with high permeation flux (high porosity) and high hydrophobicity. Thus, the effects of nonsolvent additives such as polyvinylpyrrolidone (PVP), lithium chloride, or lithium chloride mixture with small molecular organic acids (acetic acid and propionic acid) on membrane properties have been carefully studied. Emphasis has also been placed on the effects of compositions of ethanol and water coagulants (both internal and external) on the morphology of PVDF hollow-fiber membranes formed. Membrane properties in terms of its permeation, morphology, mechanical strength, pore structures, and wetting pressure have been extensively examined.

MATERIALS AND METHODS

Preparation of PVDF Hollow-Fiber Membranes

Materials

Commercially available polyvinylidene fluoride pellets Kynar® K720 and K760 (Elf Atochem, USA) were used as membrane material. The polymer was dried at 80°C for at least 8 h before its use in the preparation of spinning solutions. *N,N*-Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) (Synthesis Grade, Merck) were used as solvents, respectively. Four types of nonsolvent additives, i.e., Polyvinylpyrrolidone (PVP), lithium chloride, or lithium chloride mixture with either acetic acid (HAc) or propionic acid (PAC), was added in the spinning dope as the nonsolvent additive(s). Polyvinylpyrrolidone (PVP, K120) (GAF® ISP Technologies, Inc. $M_w = 2,900,000$), which is very well miscible with other components, i.e., PVDF, DMAc, and water, was used as an additive up to 8%. Lithium chloride (analysis grade), acetic acid (synthesis grade), and propionic acid (synthesis grade) were purchased from Merck. Ethanol (EtOH, 99.8%, Merck) or mixture of water and ethanol was used as coagulant when required. All chemicals were used without any further purification. Effects of ethanol in both internal and external coagulation fluids on the membrane morphology was studied, and the ethanol composition in water was varied between 0–100% (v/v). Tap water was used as the internal and external coagulants in hollow-fiber spinning if not specified.

Preparation of Spinning Dope

Required amount of solvent (either DMAc or NMP) and PVDF (either Kynar® K720 or K760) polymer were placed in a 1-liter wide-neck reaction flask. Initially, Heidolph RZR 2000 stirrer was set at a low speed of ~200 rpm so as to ensure thorough wetting of the polymer chip, and thus, prevent the formation of polymer lump in the later stages. Twenty minutes later, the stirrer speed was increased to ~300 rpm and dope temperature was slowly raised from 25 to 60°C using heating tape. Required nonsolvent additive(s) was then introduced to the dope solution. Dope temperature was maintained at about 60°C until all polymer chips was dissolved. Meanwhile, stirring was continued until the additives were completely dissolved. No visual turbidity was observed in all the spinning solution prepared. The

Table I Hollow-Fiber Spinning Base Conditions

Spinning Conditions	
Injection rate of internal coagulant	1.0–1.2 mL/min
Linear extrusion rate	3.8–4.6 mL/min
Nitrogen pressure	2 bar
Air gap	18 cm
Take-up velocity	~5.3 m/min
Room temperature	25 ± 1°C
Relative humidity	60%

viscosity of spinning solution was measured using Rheology International Viscometer (Model: RI: 1:M from Rheology International Ltd.) at room temperature (25 ± 1°C).

Spinning of Hollow Fibers

Then, the PVDF dope was transferred into a stainless steel tank. The solution was kept in the solution tank for 12 h to ensure proper degassing prior to spinning. The hollow-fiber spinning apparatus have been described elsewhere.²⁶ During the spinning process, the solution tank was pressurized to 2 bars using nitrogen. A tube-in-orifice spinneret with orifice diameter/inner diameter of the tube (OD/ID) of 1.0/0.38 mm was used to obtain hollow-fiber membranes. The air gap was fixed at 18 cm for all the spinning runs. The extrusion rate of the spinning solution was controlled by an adjusting valve. Water or ethanol or its mixture used as the internal coagulants was introduced at a controlled flow rate. Water or ethanol/water mixture was also used as external coagulant. Finally, hollow fibers formed were passed through a water bath to complete the solidification process and thoroughly washed in water. All nascent hollow fiber membranes were not extended by mechanical drawing, meaning that the take-up velocity of the hollow-fiber membranes was nearly the same as the free falling velocity in the coagulation bath. The resulting hollow-fiber membranes were kept in the storage tank for at least 3 days with fresh water for thorough removal of residual solvent and nonsolvent before used for further study.

All the resulting PVDF hollow-fiber membranes were dried at the ambient condition (25 ± 1°C and RH ≈ 65%). Table I shows the base spinning conditions for all batches of the hollow fibers prepared in this study.

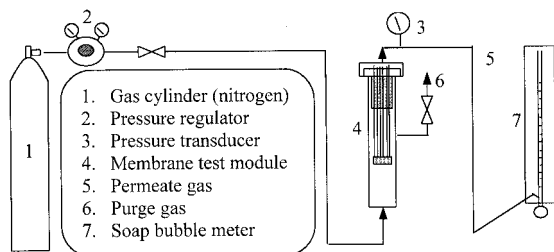


Figure 1 Schematic diagram of the gas permeation apparatus.

Membrane Characterization

Membrane Pore Size and Effective Porosity

The maximum pore radius of the resulting PVDF hollow-fiber membranes was determined using the Coulter Porometer manufactured by Coulter Electronics Ltd, UK, based on the Young-Laplace theory. In addition, the membranes were also characterized using gas permeation method suggested by Yasuda et al.³² in terms of mean pore radius (\bar{r}) and effective surface porosity ($\epsilon\tau^2$).

A test module containing six fibers with the length of approximately 6 cm each was prepared. The modules were then connected to the gas permeation apparatus as shown in Figure 1 using purified nitrogen (supplied by SOXAL Singapore, 99.9% purity) as test gas. Operating pressures were varied using pressure transducer (Basingstoke, England) in all permeation tests (22 membranes). The gas permeation flux was measured at room temperature ($25 \pm 1^\circ$) using a soap-bubble meter. Then the gas permeability coefficients were calculated at different operating pressures based on the permeation flux measured. The plots of the permeability coefficients (P) vs. average pressure ($\Delta\bar{p}$) of 22 hollow-fiber membranes are given in Figures 2 and 3, respectively. Their intercepts and slopes were used to calculate the mean pore radius as well as effective surface porosity according to equations given by Yasuda et al.³² and Cabasso et al.³³ The results are also summarized in Tables IIA and IIB.

Membrane Wetting Pressure Test

The breakthrough pressures of PVDF hollow-fiber membranes were measured by using nitrogen gas to pressurize the water through the hollow-fiber membranes in air. The test module consists of six fibers with the length of 6 cm each. Tap water was fed at the shell side of the test module, and the operating pressure was slowly increased

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. The measurements were carried out at a maximum pressure of 8 bars so as not to cause any unwanted membrane damage.

Membrane Morphology

For the preparation of specimens for SEM examination, hollow fiber membranes were first immersed in liquid nitrogen for about 2 min. Then, about 1–2-mm fiber samples were cut using a razor blade and then mounted on sample stubs. After 1 day of air drying, the samples were then coated with gold using Ion Sputtering Device (JFC-1100e). After coating, the morphology of the hollow-fiber membranes was examined using scanning electron microscope (Hitachi S-4100) at various magnifications.

RESULTS AND DISCUSSION

A total of 22 batches of PVDF hollow-fiber membranes were fabricated via the phase inversion method. The details of the polymer solutions used and the resulting hollow fibers characterized in terms of pore size and effective porosity are listed in Tables IIA and IIB. Of these, Table IIA (mem-

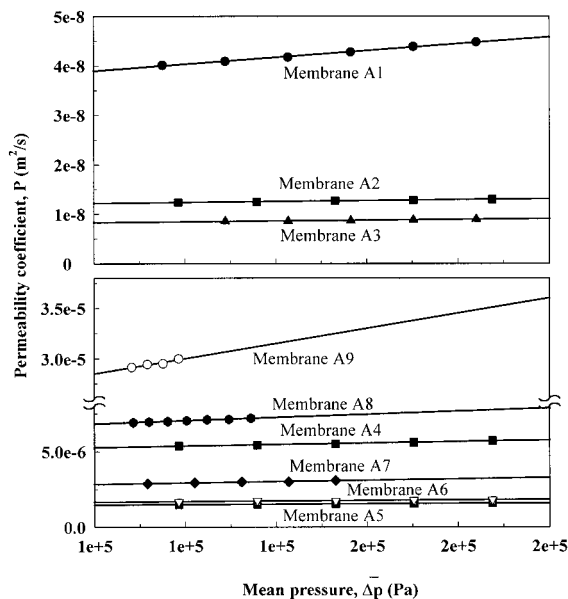


Figure 2 Permeability coefficient vs. mean pressure for membranes A1 to A9.

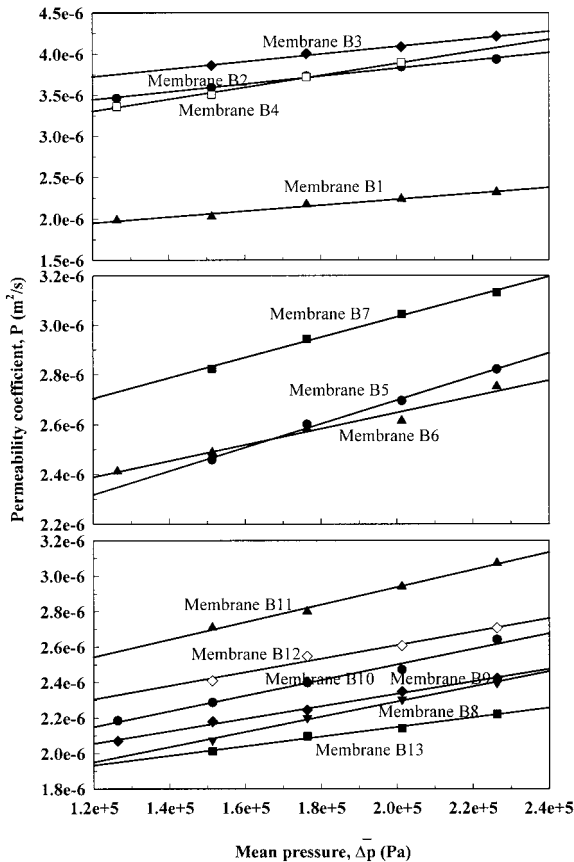


Figure 3 Permeability coefficient vs. mean pressure for membranes B1 to B13.

branes A1 to A9) summarizes the effects of PVP and coagulation mediums; while the effects of the lithium chloride and acids on the resulting membranes properties are summarized in Table IIB (membranes B1 to B13).

Effect of Nonsolvent Additives on the Membrane Characteristics

Importance of nonsolvent additive presented in dope solution lies in its influence on the following membrane properties, i.e., pore size, porosity, and morphological structure. For example, introducing a suitable nonsolvent additive into the polymer dope solution could increase the membrane porosity, which would then enhance its permeation performance. The effects of various nonsolvent additives, with special focus on its types and amount to be added into the dope solution, on the membrane properties is discussed in the following sections.

Effect of PVP as Nonsolvent Additive on the Membrane Characteristics

Nine batches of PVDF hollow-fiber membranes were prepared from polymer dopes with and without additive of PVP, as summarized in Table IIA, showing the mean pore size and the effective surface porosity obtained from the gas permeation method. The results reveal that addition of PVP has a negligible effect on the membrane mean

Table IIA Properties of the Spinning Solution and the Resulting Hollow-Fiber Membranes: Effects of PVP and Coagulation Mediums

Membrane	A1	A2	A3	A4	A5	A6	A7	A8	A9
Composition of spinning solution (wt %)									
PVDF (Kynar® K760)	20	20	20	20	20	20			
PVDF (Kynar® K720)							22	22	22
Solvent									
DMAc	80	80	80	72	72	72	70	70	70
Additive									
Polyvinylpyrrolidone (PVP-K120)	—	—	—	8	8	8	8	8	8
Coagulation mediums (water/ethanol) (v/v %)									
Internal coagulant	100/0	100/0	100/0	100/0	100/0	100/0	100/0	50/50	0/100
External coagulant	100/0	85/15	50/50	100/0	85/15	70/30	100/0	100/0	100/0
Membrane's properties									
Outer diameter (mm)	0.76	0.65	0.68	0.89	0.88	0.88	0.75	1.06	1.06
Inner diameter (mm)	0.44	0.40	0.38	0.47	0.43	0.39	0.43	0.63	0.63
Mean pore radius (μm)	0.049	0.021	0.025	0.020	0.022	0.029	0.042	0.042	0.081
Effective surface porosity, ϵ/τ^2	0.0013	0.0010	0.0006	0.4795	0.1211	0.1008	0.1118	0.2744	0.5147

Table IIB Properties of the Spinning Solution and the Resulting Hollow-Fiber Membranes: Effects of LiCl and Organic Acids

Membrane	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13
Composition of spinning solution (wt %)													
PVDF (Kynar® K760)	15	15	15	15	15	15	15	15	15	15	15	15	15
Solvent													
DMAc	85	85	85	85	85	85	85						
NMP								85	85	85	85	85	85
Additive (g/100 g solution)													
Lithium chloride (LiCl)	6	6	6	6	6	6	6	4	6	4	4	4	4
Acetic acid (HAc)	—	3	6	10	—	—	—						
Propionic acid (PAc)	—	—	—	—	2	4	6	—	—	2	4	6	8
Dope viscosity (cP)	4098	3871	3610	3310	4387	3760	3390	5084	15720	6260	5681	5020	3743
Membrane's properties													
Outer diameter (mm)	0.80	0.78	0.71	0.65	0.76	0.76	0.73	0.77	0.73	0.76	0.76	0.77	0.76
Inner diameter (mm)	0.52	0.48	0.43	0.40	0.44	0.44	0.43	0.46	0.41	0.48	0.44	0.44	0.46
Mean pore radius (μm)	0.053	0.038	0.033	0.068	0.061	0.036	0.043	0.067	0.048	0.061	0.057	0.046	0.038
Effective surface porosity, ϵ/τ^2	0.0569	0.1510	0.1923	0.0710	0.0566	0.1086	0.1019	0.0428	0.0676	0.0524	0.0676	0.0787	0.0848
Maximum pore radius (μm)	0.18	0.19	0.23	0.12	0.14	0.14	0.12	0.09	0.17	0.10	0.13	0.12	0.16

pore size, but caused a drastic increase (two order of magnitudes) in the membrane effective porosity. For instance, the effective surface porosity of membrane increases from 0.0013 (membrane A1) when no PVP added increases up to 0.4795 (membrane A4) when 8 wt % PVP was introduced into the dope solution, while their mean pore sizes are 0.049 and 0.020 μm , respectively. The same result can also be seen by comparing membranes A2 and A5, where the effective surface porosity of the membranes increases from 0.0010 (membrane A2) when no PVP added increases up to 0.1211 (membrane A5) when 8 wt % PVP was introduced into the dope solution, while their mean pore sizes are 0.021 and 0.022 μm , respectively. PVP is very well miscible with water (coagulation bath). It, thus, suggests that the rapid dimixing occurred by presence of PVP in spinning dope during the precipitation step results in thinner skin layer as well as bigger microvoids in sublayer. Therefore, considering the PVP as an organic pore-former in the polymer dopes, the increases in the permeability (Fig. 2) as well as the effective surface porosity (Table IIA) would be expected, and can be also explained by following morphology analysis.

The effects of PVP on the morphology of the resulting hollow fibers were also examined by scanning electron microscope (SEM). Figure 4 shows the SEM pictures of membranes A1 and A4 where the former was prepared from a polymer solution of 20% PVDF and 80% DMAc without PVP as nonsolvent additive, while the latter was spun from a polymer solution of 20% PVDF, 72% DMAc, and 8% PVP. Generally, the hollow fibers possess the following structural features: larger finger-like macrovoids and cavities near the outer and inner skins of the hollow fiber; the size of the macrovoids near the inner skin is much larger than those near the outer skin; finally, sponge-like structures present in between these macrovoids near the inner and outer fiber skin, i.e., at the center of the fiber wall structure.

By comparing membranes A1 and A4 (Fig. 4), the drastic effects of PVP that was added into the spinning solution of membrane A4 could be clearly seen on the structure of the membranes formed (A4) where a much larger macrovoids and cavities near both inner and outer skin are observed. Also, the thickness of the sponge-like structure at the center of the fiber wall is reduced. This is due to the hydrophilic nature of PVP caus-

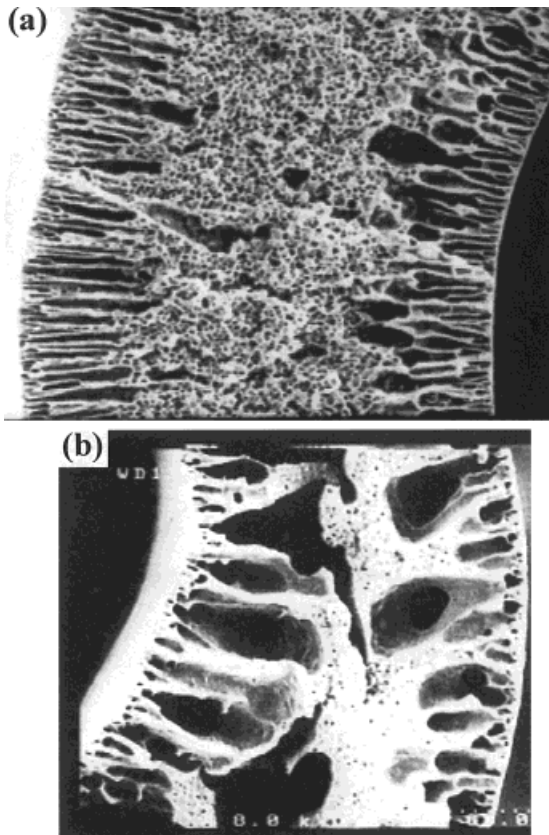


Figure 4 Scanning electron micrographs of cross-section of PVDF hollow-fiber membranes spun from 20% polymer dope. (a) no PVP; (b) 8% PVP.

ing an increase in the precipitation rate, thus, larger macrovoids and cavities were formed near both the inner and outer skin, and a thinner skin layer was obtained. As a result, lower membrane resistance and higher effective surface porosity are expected.

Although the values of the membrane effective surface porosity increased greatly following the introduction of hydrophilic polyvinylpyrrolidone (PVP) into the dope solution as a pore former, a low membrane wetting pressure of less than 3 bar was observed. This is due to the existence (could not be washed away completely) of high molecular weight hydrophilic PVP in the hollow fibers, which reduces the membrane hydrophobicity. This property is certainly not desirable for the membrane-based gas absorption application if the liquid absorbent needs to be operated at the elevated pressure.

Effects of Lithium Chloride and Acid as Nonsolvent Additives on the Membrane Characteristics

As mentioned in the previous section, the prime objective of this study is to produce PVDF hollow

fiber membranes with higher porosity as well as excellent hydrophobicity. To fulfill these objectives, inorganic salt of small molecular weight, i.e., LiCl, was employed as additive in the preparation of the PVDF hollow-fiber membranes. However, it should be noted that high LiCl content in the polymer solution might result in a gelled dope.¹⁸ Generally, the maximum amount of LiCl added to 100 g binary solution was 5 g for the PVDF–NMP system and 10 g for the PVDF–DMAc system.¹⁸ Additionally, small molecular weight organic acids (acetic acid and propionic acid) were also used as nonsolvent additives in the PVDF–solvent–LiCl system to further increase the porosity of the PVDF hollow-fiber membranes.

In this work, hollow-fiber membranes were spun from polymer solution containing 15 wt % PVDF (K-760) in 85 wt % solvent (either DMAc or NMP). Undoubtedly, membranes with high permeation flux could be obtained from dope solution with low polymer concentrations. However, the viscosity of this low polymer spinning solution is often too low, i.e., far less than several thousands centipose, which is generally required for the ease of the hollow-fiber spinning procedure. This problem could be overcome by introducing lithium chloride (LiCl) into the dope solution. Apart from increasing the solution viscosity, LiCl also acts as a good pore former. Figure 5 shows the relationship between the dope solutions viscosity and the amount of LiCl added. A nonlinear increase in the dope solution viscosity was observed corresponding to the amount of LiCl added. This could be due to the strong interactions between LiCl and solvent. Also, it is evident that a much faster viscosity increase was observed in the case where NMP

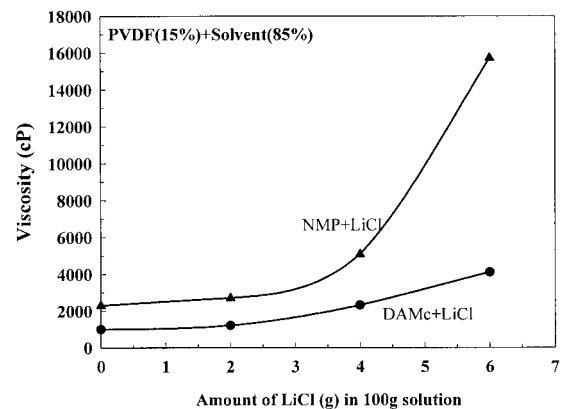


Figure 5 Effect of the amount of LiCl on the viscosity of PVDF–DMAc and PVDF–NMP solutions.

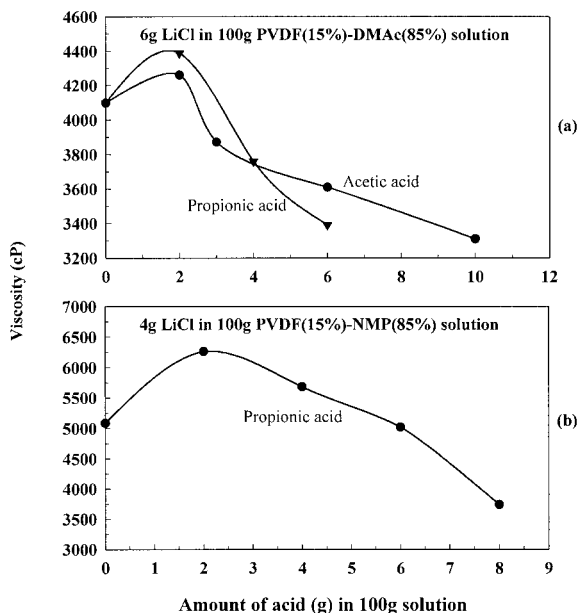


Figure 6 Effect of the amount of acids on the solution viscosity (a) 6 g LiCl in 100 g PVDF–DMAc solution; (b) 4 g LiCl in 100 g PVDF–NMP solution.

was used as solvent. For instance, the solution viscosity of 3600 cP was detected following the addition of 6 g LiCl into 100 g DMAc–PVDF binary solution, while the solution viscosity as high as 5084 cP was measured when 4 g LiCl was added into 100 g NMP–PVDF binary solution (Fig. 5).

The effects of the quantity of acid added in the spinning dope on the viscosity were also examined. Figure 6 shows the variations in solution viscosity with the addition of acid (acetic acid or propionic acid) into the PVDF–LiCl–solvent ternary system. It can be seen in Figure 6(a) and (b) that there is an increase in the viscosity of spinning solutions, followed by a sharp decrease with the addition of acids. This implies the existence of a maximum viscosity value with respect to the amount of acetic acid or propionic acid added as a nonsolvent additive. The initial viscosity increase may be due to the strong acid–solvent interactions, i.e., formation of Lewis acid complex between acid and solvent, which may decompose instantly on coming in contact with water in the hollow-fiber formation process. However, further addition of acid into the solution may, in turn, dilute the polymer solution, hence, resulting in a decreased solution viscosity.

Membrane geometry, both maximum and mean pore radius as well as effective surface porosity of the hollow-fiber membranes, are listed in

Table IIB. The outer diameters of the hollow fibers range from 0.65 to 0.80 mm, with a wall thickness of 0.13 to 0.17 mm. The maximum pore radius of all the batches of the hollow-fiber membranes were found to be around 0.15 μm except for membrane B3, with the biggest pore radius of 0.23 μm . It should be noted that correlation between the condition of membrane preparation and the maximum pore radius could hardly be drawn. However, the addition of certain amount of acids in the spinning dope generally can cause the increase of the membrane permeability, as shown in Figure 3. From Table IIB, it can be concluded that the maximum pore radius of the hollow fiber produced was nearly unaffected by the increased amount of acid added into the PVDF–solvent–LiCl spinning solution. At the absence of the acids, the maximum pore radius, however, seems to increase with increasing amount of LiCl added into spinning solution. By comparing membranes B8 and B9 or B1, it was noticeable that an additional amount of 2 g of LiCl being added into 100 g binary solutions causes the maximum pore radius to increase from 0.09 to 0.17 or 0.18 μm , which was almost two times larger. The larger maximum pore radius is not desirable for membrane-based gas absorption, as a bigger pore radius could be easily wetted during the operation, thus resulting in a poor mass transfer rate. To conclude, addition of acid into the spinning solution is of preference in our attempts to produce hollow fiber with higher porosity due to least interference with a maximum pore radius of membrane produced.

With reference to Table IIB, not much variation was observed in terms of the mean pore radius of the spun hollow-fiber membranes with the addition and quantity of acid introduced into the spinning solution. However, experimental data presented in Table IIB further reveals that the effective surface porosity of the resulting PVDF hollow-fiber membrane increased more significantly in systems using acid (acetic acid or propionic acid) as the nonsolvent in the PVDF–solvent–LiCl system. For example, the porosity of membranes B1 and B2 increases from 0.0569 to 0.1510 when 3 g acetic acid was introduced into the 100-g spinning dope, which is almost three times larger in the porosity value. Data in Table IIB also indicates that the effective surface porosity of the hollow-fiber membrane prepared from HAc–LiCl–PVDF–DMAc system is higher than those produced from PAc–LiCl–PVDF–DMAc or PAc–LiCl–PVDF–NMP system. For instance, the

porosity of membrane B1 increased from 0.0569 to 0.1086 (membrane B6) when 4 g propionic acid was employed in 100 g spinning dope, which was only two times larger in porosity value. This suggests that the presence of acetic acid in the spinning solution would result in the membrane with higher effective porosity.

Further inspection of the data in Table IIB reveals that there exists an optimum amount of acid added into the LiCl–PVDF–DMAc system, at which a maximum value of effective surface porosity is possible. For example, the maximum porosity value of 0.1923 is achieved when 6 g acetic acid was employed in 100-g spinning dope. However, such a maximum value could not be observed for the LiCl–PVDF–NMP system.

The effects of acids on the morphology of the resulting hollow fibers were also examined by scanning electron microscope (SEM). Figure 7(a), (b), and (c) shows the cross-sectional structures of PVDF hollow-fiber membranes produced from the PVDF–LiCl–DMAc system with addition of 0, 3, or 10 g of acetic acid in 100-g polymer solution, respectively. Basically, there is no distinct difference in terms of membrane morphology for the hollow-fiber membranes formed in the presence or absence of acid as nonsolvent additive. The membrane B4 [Fig. 7(c)] produced from the spinning dope with a higher amount of acetic acid shows a thicker sponge layer, which results in an increased dead volume, hence showing reduced effective surface porosity, as shown in Table IIB. The PVDF hollow-fiber membranes fabricated using acid as the nonsolvent has, however, better mechanical strength compared to those produced using PVP, as shown in Figure 4(b) due to the less alteration in its microvoids structures.

As for the wetting pressure test, all batches of hollow-fiber membranes could withstand a pressure up to 8 bars with no occurrence of water breaking through. Obviously, the hydrophobicity of these PVDF hollow-fiber membranes is much higher than those produced by using PVP as additive. Thus, making it a viable choice in membrane based gas absorption process as it could eliminate the wetting problem during operation.³⁴

Effects of Coagulation Mediums on the Membrane Characteristics

The effects of internal and external coagulation mediums on the hollow fibers were investigated using ethanol or its mixture with water in the

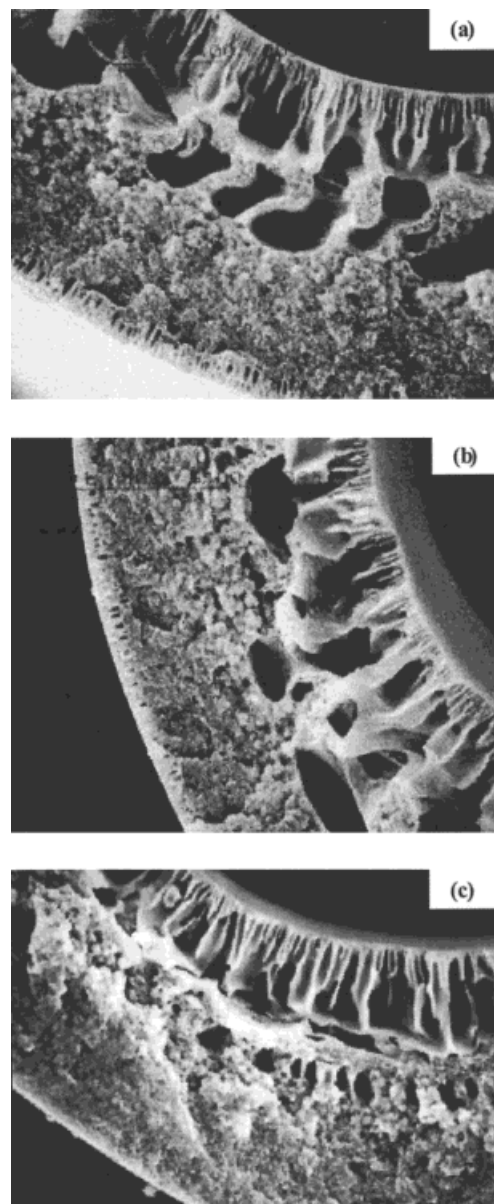


Figure 7 Scanning electron micrographs of cross-section of PVDF hollow-fiber membranes spun from 15% polymer, 85% DMAc dope containing different amount of acetic acid. (a) 0; (b) 3 g/100 g dope; (c) 10 g/100 g dope.

coagulation bath to control the locality of the skin in the resulting PVDF hollow-fiber membranes. In general, the thin membrane skin may be located either at the inner or outer skin wall, depending on the properties of the internal and external coagulants used. SEM micrographs of the spun hollow-fiber membranes (membranes A7, A3, and A9) for three typical coagulation conditions were shown in Figure 8. With this, the

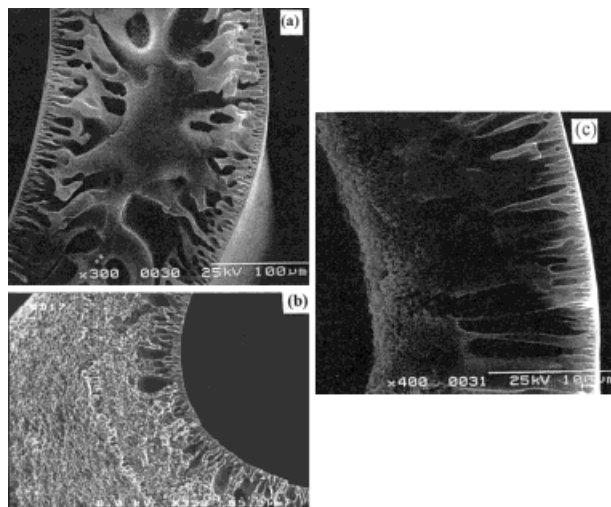


Figure 8 Scanning electron micrographs of cross-section of PVDF hollow fibers coagulated in (a) internal: water; external: water; (b) internal: water; external: 50% (vol.) ethanol in water; (c) internal: ethanol; external: water.

dependence of skin location on coagulation medium is clearly demonstrated. The fiber structure (membrane A7) with both inner and outer skins, as shown in Figure 7(a), could be attributed to the rapid precipitation occurring at both the inner and outer fiber walls when water, a strong nonsolvent, is used as both the internal and external coagulants. When a substantial amount of ethanol (50 vol % ethanol in water) was added into the external water coagulation bath, the precipitation rate in the outer wall of the fiber (membrane A3) is greatly reduced with external skin being completely eliminated [Fig. 7(b)]. Similarly, the inner fiber skin (membrane A9) can also be completely removed when pure ethanol was used as the internal coagulant due to drastic precipitation rate reduction as shown in Figure 7(c). By retaining only one of the skins in the hollow-fiber membrane, the permeability value may, therefore, be increased. However, as shown Figure 2, this is only true for the ethanol or its mixture used as the internal coagulant (membranes 7–9). When the ethanol mixture was used as external coagulant (membranes A1–A3 or membranes A4–A7), the reverse trends were observed. The reason for such a contrary result is due to the other factors simultaneously affecting the membrane permeability. As the slow precipitation eliminates the asymmetric skin (decrease of membrane thickness), it may also increase the formation of dead pores (decrease of ϵ). These two reverse effects

would either increase or decrease the membrane permeability, depending on which one is the dominating factor. Figure 9 further confirms that the increased ethanol concentration in external coagulation bath leads to a shift in the membrane morphology from large cavities to sponge-like stricture near the outer skin of the fibers. It is, therefore, conceivable that the membrane permeability decreases with increase of ethanol concentration in the external coagulant, as formation of the sponge-like structure (dead pores) becomes the dominating factor.

CONCLUSION

Polyvinylidene fluoride hollow-fiber membranes were prepared using lithium chloride and acid as nonsolvents via a phase inversion technique. In this study, PVP was found to be a good pore former, resulting in the PVDF hollow-fiber mem-

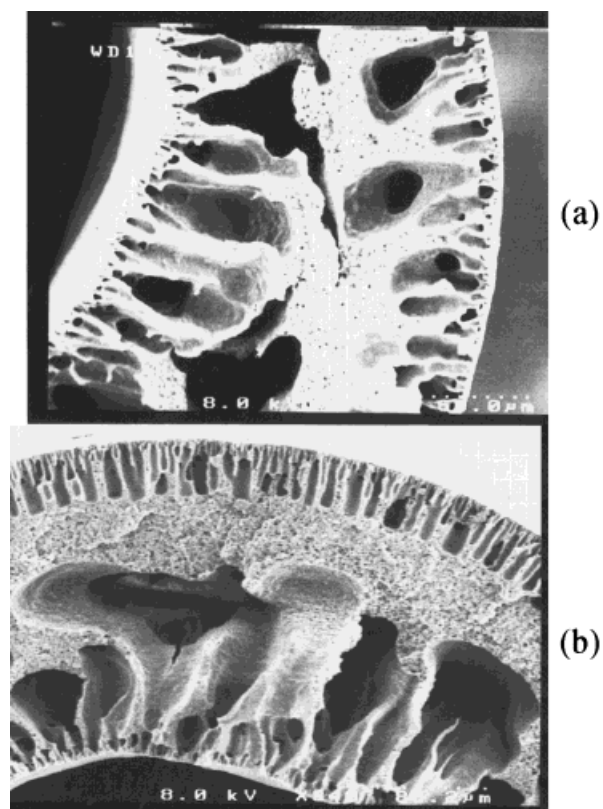


Figure 9 Scanning electron micrographs of cross-section of PVDF hollow-fiber membranes spun from a polymer dope consisting of 20% PVDF, 8% PVP, and 72% DMAc using different external coagulants: (a) water; (b) 15% (vol.) ethanol in water.

branes with higher porosity, however, with lower hydrophobicity. Besides, experimental results also showed that the presence of lithium chloride and acid mixture in the spinning solution is capable of producing hollow-fiber membranes with higher porosity. Negligible alteration on the maximum pore radius was observed with the amount of acid added into the spinning solution. The use of acetic acid (HAc) as the nonsolvent in the PVDF-DMAc-LiCl system would give a higher effective surface porosity compared to PAc-LiCl-PVDF-DMAc or PAc-LiCl-PVDF-NMP systems. The results also show that there is an optimum cutoff point for the amount of acid to be added to obtain a maximum porosity, of which further addition of acid into the spinning solution would cause a decrease in the porosity value. Moreover, using the ethanol as the internal coagulant during the spinning process can eliminate the inner skin, thus resulting in a higher membrane permeability.

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REFERENCES

- Sirkar, K. K. In *Membrane Handbook*; Ho, W. S. W.; Sirkar, K. K. Eds.; Van Nostrand Reinhold: New York, 1992; p. 885.
- Unno, H.; Saka, H.; Akehata, T. *J Chem Eng Jpn*, 1986, 19, 281.
- Daiminger, U.; Nitsch, W.; Plucinski P.; Hoffmann, S. *J Membr Sci* 1995, 99, 197.
- Halavacek, M. *J Membr Sci* 1995, 102, 1.
- Tirmizi, N. P.; Raghuraman, B.; Wiencek, J. *AIChE J* 1996, 42, 1263.
- Schneider, K.; Van Gassel, T. S. *Chem Eng Technol* 1984, 56, 514.
- Schofield, R. W.; Fane, A. G.; Fell, C. J. D. *J Membr Sci* 1987, 33, 299.
- Castro, A. J. U.S. Pat. 4,247,498 (1981).
- Chlubek, N.; Tomaszewska, M. *Environ Protein Eng* 1989, 15, 95.
- Dohany, J. E.; Robb, L. E. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 1980, p. 64, 3rd ed., vol. 11.
- Lovinger, A. J. In *Development in Crystalline Polymers*; Bassett, D. C. Ed., Applied Science: London, 1982, p. 195, vol. 1.
- Sugihara, M.; Fujimoto, M.; Uragami, T. *Polym Prepr Am Chem Soc Div Polym Chem* 1979, 20, 999.
- Uragami, T.; Fujimoto, M.; Sugihara, M. *Polym Prepr Am Chem Soc Div Polym Chem* 1980, 21, 21.
- Uragami, T.; Naito Y.; Sugihara, M. *Polym Bull* 1981, 4, 617.
- Bottino, A.; Capannelli, G.; Munari, S. *Polymer* 1980, 21, 21.
- Bottino, A.; Capannelli, G.; Munari, S. *J. Appl Polym Sci* 1985, 30, 3009.
- Bottino, A.; Capannelli, G.; Munari, S. In *Membrane and Membrane Processes*; Drioli, E.; Nakagaki, M., Eds.; Plenum Press: New York, 1986, p. 163.
- Bottino, A.; Capannelli, G.; Munari, S.; Turturro, A. *Desalination* 1988, 68, 167.
- Bottino, A.; Camer-Roda, G.; Capannelli, G.; Munari, S. *J Membr Sci* 1991, 57, 1.
- Shih, H.-C.; Yeh, Y.-S.; Yasuda, H. *J Membr Sci* 1990, 50, 299.
- Benzinger, W. D.; Robinson, D. N. U.S. Pat. 4,384,047 (1983).
- Munari, S.; Bottino, A.; Camera-Roda, G.; Capannelli, G. *Desalination* 1990, 77, 85.
- Fuji, T. N.; Kawasaki, T. Y. U.S. Pat. 4,399,035 (1983).
- Doi, Y. Eur. Pat. 0,378,441 (1990).
- Danville, R. D. M.; Antioch, R. A. L. U.S. Pat. 5,013,339, 1991.
- Wang, D. Ph.D Thesis, Department of Chemical Engineering, National University of Singapore, 1995.
- Cabasso, I.; Klein, E.; Smith, J. K. *J Appl Polym Sci* 1977, 21, 165.
- East, G. C.; McInture, J. E. V.; Rogers, S. C. S. In *Proceeding of the Fourth BOC Priestley Conference (Leeds)*, Royal Society of Chemistry, London, UK, 1986.
- Ekiner, O. M.; Vassilatos, G. *J Membr Sci* 1990, 53, 259.
- Smid, J.; Albers, J. H. M.; Kusters, A. P. M. *J Membr Sci* 1991, 64, 121.
- Wang, D.; Li, K.; Teo, W. K. *J Membr Sci* 1996, 115, 85.
- Yasuda, H.; Tsai, J. T. *J Appl Polym Sci* 1974, 18, 8005.
- Cabasso, I.; Robert, K. Q.; Klein, E.; Smith, J. K. *J Appl Polym Sci* 1977, 21, 883.
- Li, K.; Kong, J. F.; Wang, D.; Teo, W. K. *AIChE J* 1999, 45, 1211.