Fabrication of 6FDA-Durene Polyimide Asymmetric Hollow Fibers for Gas Separation

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ABSTRACT: We have developed defect-free asymmetric hexafluoro propane diandydride (6FDA) durene polyimide (6FDA-durene) hollow fibers with a selectivity of 4.2 for O_2/N_2 and a permeance of 33.1 $\times 10^{-6}$ cm^3 (STP)/cm^2-s-cmHg for O_2. These fibers were spun from a high viscosity *in situ* imidization dope consisting of 14.7% 6FDA-durene in a NMP solvent and the inherent viscosities (IV) of this 6FDA-durene polymer was 0.84 dL/g. Low IV dopes cannot produce defect-free hollow fibers, indicating a 6FDA-durene spinning dope with a viscosity in the region of chain entanglement seems to be essential to yield hollow fibers with minimum defects. The effects of spinning parameters such as shear rates within a spinneret and bore fluids as well as air gap on gas separation performance were investigated. Experimental data demonstrate that hollow fibers spun with NMP/H_2O as the bore liquid have higher permeances and selectivities than those spun with glycerol as the bore liquid because the former has a relatively looser inner skin structure than the latter. In addition, the selectivity of hollow fibers spun with NMP/H_2O as the bore liquid changes moderately with shear rate, while the selectivity of hollow fibers spun with glycerol are less sensitive to the change of shear rate. These distinct behaviors are mainly attributed to the different morphologies generated by different bore fluids. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2166–2173, 2001

Key words: 6FDA-durene polyimide; asymmetric hollow fiber; gas separation; defective-free; shear rate; bore fluid effects

INTRODUCTION

Membrane-based gas separation processes have been recognized as effective and economical ap-

proaches in some applications of gas treatments, such as the recovery of H_2 from industrial gas mixture of CH_4, N_2, or CO_2, the purification of natural gas, and the enrichment of either O_2 or N_2 from air. To yield successful membrane processes, advances in both membrane materials with superior separation properties and fabrication technology are required.

During past 2 decades, significant progress has been made in membrane materials. Polyimides, particular hexafluoro-modified polyimides, have been identified as promising materials for gas separation due to their excellent separation char-

acteristics and high inherent thermal stability as well as mechanical strength.[1–3] Asymmetric hollow fibers fabricated from polyimide synthesized from hexafluoro propane diandydride (6FDA) with 3, 3′-6FDA-diamine,[4] 4, 4′-6FDA-diamine,[5] and durene diamine[6,7] with impressive separation performance have been demonstrated for air separation. Multilayer composite membranes using 6FDA-polyimides as the gutter layer as well as the selective layer have also been developed.[8–11] 6FDA-durene polyimide is of high-performance fluoropolyimides, which have an impressive permeability with a reasonable selectivity.[5,7,12–13] Polyimide made of 6FDA and 1, 3-phenylenediamine (mPDA) also has an attractive separation performance and other desirable properties.[14,15]

Membrane fabrication technology also advanced significantly with the development of new materials during the last 2 decades. In fact, without a breakthrough in fabrication, the applications of newly invented high-performance membrane materials would be very limited. Several major advances in membrane fabrication took place in the last 2 decades, for example, Permea's gradient dense-layer membranes,[16,17] Koros group's defect-free ultrahigh flux asymmetric membranes,[18,19] and Chung et al.'s ultrathin high-performance hollow fiber membranes and multilayer composite membranes.[10,20–23]

However, fabrication of asymmetric hollow fibers with superior permeability and selectivity is still a challenging subject. To achieve excellent gas separation performance, the selective layer of asymmetric hollow fibers must be almost defective free with a surface defect ratio of less than 10^{-5}. Because the spinning of hollow fibers involves many controlling factors, such as the preparation of polymer dope, the chemistry of both bore fluid and external coagulant, spinning conditions, as well as the dimensions of the spinneret used, all the influences by various factors should be taken into consideration.

Chung and his coworkers were pioneers in developing defect-free 6FDA-polyimide hollow fibers with a selectivity of 4.3–5.1 for O_2/N_2 and an average permeance of 240 GPU for O_2.[5] They spun fibers directly from in situ polymerization dope and completely eliminate the complicated and time-consuming process of dope preparation. However, their work was mainly focused on air separation and the effect of shear rate on fiber formation and performance was not studied. Chung et al. later studied the shear rate effect on

6FDA-polyimide hollow fibers using a relative low IV polymer (0.5 dL/g) on various gases,[7] and found that the shear rate affected the separation performance of 6FDA-durene hollow fiber membranes similar to those reports on polysulfone type gas separation membranes[24] and ultrafiltration membranes.[25,26] Because the polymer they used had a low IV, the as-spun 6FDA-polyimide hollow fibers were defective and has to be coated with silicone rubber to provide the selectivity. They observed that shear induced chain orientation and enhanced chain package, thus increasing selectivity and reducing permeance. On the other hand, the shear thinning characteristics of their dope induced skin defects at high shear rates and thus reduced selectivity and increased permeance. Shilton et al.[27] also studied shear effects and reported some similar as well as different results from Chung et al.'s work because the former used dry-jet wet spinning, while the latter employed wet spinning.

The purpose of this article is to reexamine the effects of spinning conditions and shear rate on the formation of defect-free 6FDA-durene polyimide asymmetric hollow fibers and their separation performance using relatively high IV materials. We also investigate the effect of bore fluid chemistry on fiber morphology and separation performance. The hollow fiber membranes developed here are defect free, which is quite distinct from the previous work[7] and the bore fluid and external coagulant used to develop these defect free membranes is also quite different from the previous work.[5]

EXPERIMENTAL

Materials

6FDA-durene polyimide was chosen as the dope material because it has high permeability and reasonable selectivity based on the characterization of its dense film as illustrated in Table I. The 6FDA-durene in situ dope formulation was synthesized in our lab by using a process as described in Chung et al.'s patent.[28] Polyamic acid was synthesized using a solution polycondensation reaction of 50 mol % 6FDA and 50 mol % durene diamine. It was then imidized by adding specific amounts of propionic anhydride and β-picoline to the solution and reacted for another 17–19 h. Because most propionic anhydride was converted to propionic acid (PA) during imidization by wa-

Table I Permeability and Selectivity of 6FDA–Durene Polyimide Dense Films

Permeability (Barrer[a])				Ideal Selectivity		
He	O_2	N_2	CO_2	CO_2/N_2	O_2/N_2	He/N_2
379	118	32	380	110.9	3.7	11.8

Film thickness = 42.1 μm, temperature = 35°C, pressure = 10 atm.
[a] 1 Barrer = 1×10^{-10} cm^3 (STP) · cm/cm^2-s-cmHg.

ter, a by-product, one would obtain an *in situ*-imidized 6FDA-durene dope in a NMP/PA/β-picoline/propionic anhydride solution directly from polymerization. The inherent viscosities (IV) of two batch dopes are 0.64 and 0.84 dL/g, respectively. The number average molecular weight (M_n) determined by GPC for the 0.64 dL/g IV dope is 49,193. For the 0.84 dL/g IV dope, the M_n is 71,291. *N*-methyl-2-pyrrolidone (NMP, >99%) was supplied by MERCK. Glycerol and methanol were purchased from MERCK and used as received.

Viscosity Measurements of 6FDA-Durene Dopes

Using an ARES Rheometric Scientific rheometer, we determined the shear stress of the dope solution as a function of shear rate. The experiment was conducted utilizing a 25-mm cone-plate at 26°C and the steady-state shear was measured in the range of 0.1 to 100 s^{-1}. The rheological data were fitted by a power-law model and a relationship between shear stress τ (dyn/cm^2) and shear rate γ (s^{-1}) was obtained as follows:

$$\tau = m|\dot{\gamma}|^n \tag{1}$$

and the viscosity (μ) of 6FDA-durene dopes was calculated as follows.

$$\mu = m|\dot{\gamma}|^{n-1} \tag{2}$$

where m and n are constants. The experiments were carried out in room temperature (at about 26°C). The above equation was assumed to be appropriate to describe the rheological behavior of the dope solution within the spinneret during spinning at higher shear rates. By applying the axial annular flow of a power-law fluid, one may calculate the shear rate and shear stress of the spinning dope near the external wall of the annular region within a spinneret.[29,30]

Spinning Device and Conditions

Figure 1 shows the schematic diagram of the hollow fiber spinning apparatus. The formulated dope was conveyed under nitrogen pressure, and bore fluid was delivered by an ISCO 500D syringe pump. This ISCO precision pump has an accuracy of ±0.5% flow rate. The spinning dope and the bore fluid came across at the exit of the spinneret then entered the coagulation bath. Both wet-spinning and dry-jet wet spinning processes were used. Upon precipitation, all the nascent fibers produced were taken up without extra drawing. The as-spun fibers were rinsed in flowing water at room temperature for more than 24 h, then immersed in methanol twice for more than 1 h, finally dried in the air for more than 24 h before test. The detailed process parameters and the shear rates as well as bore fluids used are listed in Tables II and III.

Measurement of Separation Performance

To determine the permeance of hollow fiber membranes, three or four dried fibers with a length of about 10–15 cm were assembled into a bundle to make a simple module. H_2, O_2, N_2, and CO_2 were tested in sequence at 50 psi. Gas permeation rate was determined with a bubble flow meter. The
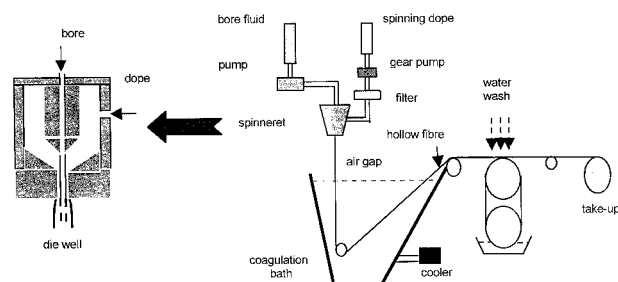

Figure 1 Schematic diagram of a hollow fiber spinning line.

Table II   Spinning Conditions of 6FDA–Durene Asymmetric Hollow Fibers (Batch 1)

Polyimide Dope	14.7% 6FDA–Durene in NMP IV = 0.64 dL/g M_n = 49,193
Bore fluid	NMP/H_2O (2/1 wt/wt)
External coagulant	Water
Spinning rate	0.701 g/min
Bore fluid flow rate	0.35 mL/min
Air gap	0 or 30 mm
Spinning temperature	Room temperature
L/(OD-ID)	11.7
OD/ID	0.8 mm/0.5 mm

permeance (P/L) is calculated by the following equation:

$$\frac{P}{L} = \frac{Q}{\Delta PA} = \frac{Q}{n\pi Dl\Delta P} \qquad (3)$$

where P = permeability of the separation layer (Barrer); L = thickness of selective layer (cm); Q = the gas flux reading (cm^3/s); ΔP = transmembrane pressure drop (cmHg); A = membrane effective surface area (cm^2); n = number of tested fibers; D = outer diameter of the fibers (cm); l = effective length of the fibers (cm). GPU was used as the gas permeation units, and one GPU is equal to 1×10^{-6} cm^3 (STP)/cm^2-s-cmHg.

The ideal separation factor of an asymmetric membrane for gases A and B can be determined from the following equation:

$$\alpha = (P/L)_A(P/L)_B \qquad (4)$$

Characterization of Membranes Morphology by SEM

Membrane samples for Scanning Electron Microscope (SEM) study were immersed in liquid nitrogen, fractured, and then sputtered with gold using JOEL JFC-1100E Ion Sputtering Device. Both a JOEL® JSM U3 electron microscope and a field emission scanning electron microscope Hitachi® S-4100 were employed to investigate fiber morphology.

RESULTS AND DISCUSSION

Viscosity of 6FDA-Durene Dopes

For the 0.64 dL/g 6FDA-durene dope (referred as the batch 1), its viscosity varies from 100×10^3 cP

to 4×10^3 cP when shear rate increases from 0.3 to 100 s^{-1}, while for the 0.84 dL/g dope (batch 2), its viscosity changes from 300×10^3 cP to 20×10^3 cP when shear rate increases from 0.1 to 100 s^{-1}. This dope shows shear thinning characteristics. The average values of m and n constants of this dope are 1159 dyn/cm^2.s^n and 0.5658, respectively.

Performance of 6FDA-Durene Asymmetric Hollow Fibers Spun from the Batch 1 Dope

Table IV summarizes the performances of 6FDA-durene asymmetric hollow fiber membranes spun from the batch 1 dope with both wet-spinning and dry-jet wet spinning conditions, respectively. This table clearly demonstrates that air-gap plays a very important role on nascent fiber performance. The permeances of all gases measured increase greatly when an air gap of 30 mm is employed in the spinning process. The increase in permeance is probably due to the fact that air gap introduces an elongational stress on fibers because of gravity. This stress may either give rise to chain orientation (i.e., reduce permeance) or defects (i.e., increase permeance) at the dense selective layer depending on the dope rheology, polymer molec-

Table III   Spinning Conditions of 6FDA-Durene Asymmetric Hollow Fibers (Batch 2)

Polyimide Dope	14.7% 6F–Durene in NMP IV = 0.84 dL/g M_n = 71,291
Bore fluid flow rate/dope flow rate	0.5 (wt/wt)
External coagulant	Water
Air gap (mm)	0 (wet spinning)
Spinning temperature	Room temperature
L/(OD-ID)	11.7
OD/ID	0.8 mm/0.5 mm

Run No.	Spinning Pressure (psi)	Bore Fluid	Shear Rate (s^{-1})
1	35.9	glycerol	461
2	70.1	glycerol	1096
3	81.6	glycerol	1544
4	93.0	glycerol	2067
5	35.7	NMP/H_2O (2/1)	461
6	70.0	NMP/H_2O (2/1)	1096
7	81.0	NMP/H_2O (2/1)	1544
8	93.4	NMP/H_2O (2/1)	2067

Table IV Performances of 6FDA–Durene Asymmetric Hollow-Fiber Membranes (Batch 1)

	Permeance (GPU[a])	
	Air Gap = 0 mm	Air Gap = 30 mm
H_2	679	3656
O_2	168	1089
N_2	54	489
CO_2	514	3148
	Selectivity	
CO_2/N_2	9.5	6.4
O_2/N_2	3.1	2.2
H_2/N_2	12.6	7.5

Test temperature: room temp.
Test pressure: 50 psig.
[a] 1 GPU = 1×10^{-6} cm^3 (STP)/cm^2-s-cmHg.

ular weight, dope formulation, and the magnitude of the elongational stress.[31,32] Because this fiber is made from a medium IV material, the newly formed skin selective layer may have weak mechanical strengths, and thus it cannot afford the stress induced by the air gap and the nascent outer skin becomes defective.

However, wet-spun 6FDA-durene fibers still possess a reasonable high selectivity for each pair of gases, indicating the existence of much less defects on the selective layer. These defects are mainly caused by two factors; the 6FDA-durene has a relatively low IV, and the spinning dope has

low viscosity characteristics. These experimental results imply that a spinning dope with a viscosity in the region of chain entanglement seems to be essential to yield hollow fibers with minimum defects, as suggested in the literature.[4,20]

Performance of Defect-Free 6FDA-durene Asymmetric Hollow Fiber Membranes Spun from the Batch 2 Dope

Table V lists the performances of 6FDA-durene asymmetric hollow fiber membranes obtained from using the batch 2 dope. The effects of shear rate and bore fluid on the performance of 6FDA-durene asymmetric hollow fibers were investigated. The hollow fibers spun with NMP/H_2O (2 : 1 weight ratio) as the bore liquid have higher permeances and selectivities than those spun by using glycerol as the bore liquid. No matter which bore fluid is employed, all fibers have O_2/N_2 selectivities more than 3.4 and CO_2/N_2 selectivities more than 21. Based on these performances, these fibers seem to have almost defect-free selective skin layer because of a high IV and high viscous dope used, which has been verified by their SEM pictures.

In the case of hollow fibers spun using glycerol as the bore liquid, their permeances decrease monotonically with an increase in shear rate, while hollow fibers spun replacing NMP/H_2O (2 : 1 weight ratio) as the bore liquid show an up-and-down relationship between permeance and shear rate. Once the shear rate is greater than 1096 s^{-1}, all fibers show decreasing permeance with in-

Table V Separation Performance of 6FDA–Durene Asymmetric Hollow-Fiber Membranes (Batch 2)

	Permeance (GPU[a])							
Run No.	1	2	3	4	5	6	7	8
H_2	127	115	115	90.8	166	225	161	151
O_2	28.3	27.3	24.9	20.2	33.1	44.0	26.7	22.7
N_2	7.6	8.1	6.8	5.8	7.9	11.5	6.7	4.9
CO_2	171	170	152	122	228	268	158	132
	Selectivity							
CO_2/N_2	22.5	21.0	22.4	21.0	28.9	23.3	23.6	26.9
O_2/N_2	3.7	3.4	3.7	3.5	4.2	3.8	4.0	4.6
H_2/N_2	16.7	14.2	16.9	15.7	21.0	19.6	24.0	30.8

Calculated skin thickness: 2.9 μm (No. 8).
Test temperature: room temp.
Test pressure: 50 psi.
[a] 1 GPU = 1×10^{-6} cm^3 (STP)/cm^2-s-cmHg.

(a) cross section

(b) cross section (magnify)

(c) cross section (near outer)

(d) cross section (near inner)
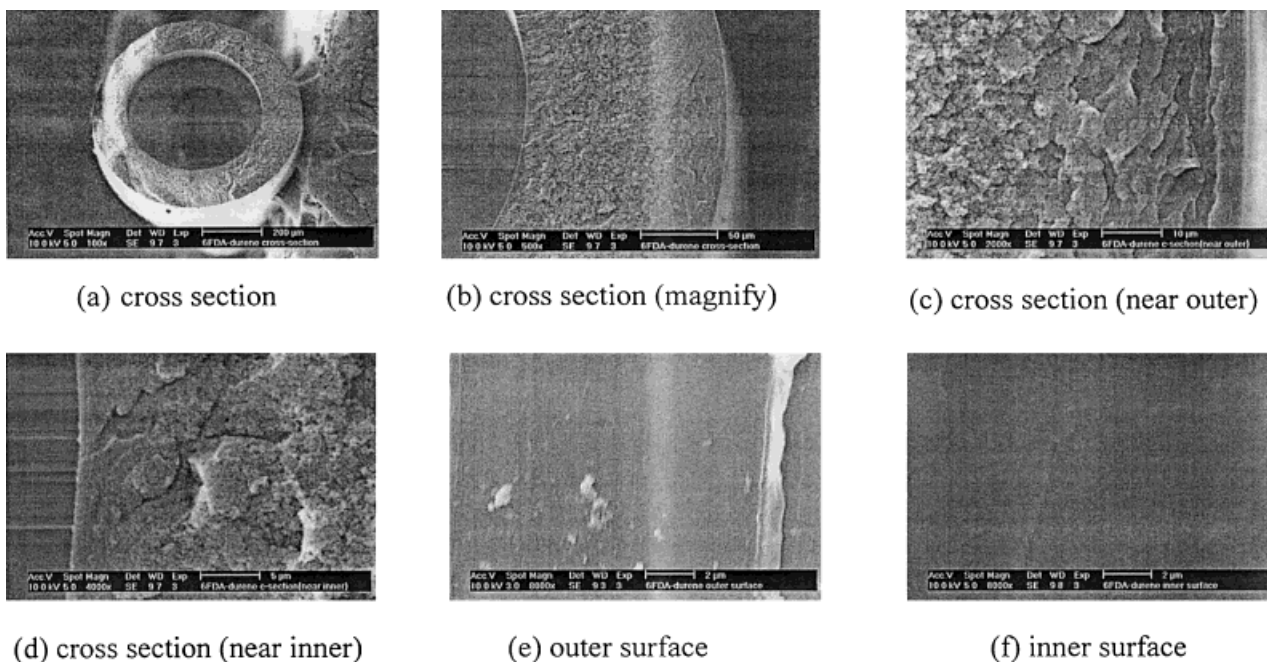

(e) outer surface

(f) inner surface

Figure 2 SEM pictures of hollow fibers (run No. 1 in Table V).

creasing shear rates probably caused by shear induced molecular orientation and chain packaging.[24] Because the batch 2 dope has a much higher inherent viscosity IV (0.84 dL/g) and less shear thinning characteristics than that (IV = 0.5 dL/g) used in the previous work,[7] the relationship between permeance and shear rate in the current study seems to be less complicated. For readers' information, the low IV (0.5 dL/g) dope utilized in the previous work yield defective skin hollow fibers that complicated the effect of shear rate on fiber performance.[7]

It is also found that the selectivities of hollow fibers spun with NMP/H_2O (2 : 1 weight ratio) as the bore liquid change modestly with shear rate. In contrast, the selectivities of hollow fibers spun with glycerol as the bore liquid are less sensitive to the change of shear rate. This may be a result from the dual skin structures on both outer and inner surfaces of hollow fibers spun using glycerol as the bore liquid, while the hollow fibers spun with NMP/H_2O (2 : 1 weight ratio) as the bore liquid has single dense skin structure on the outer surface of hollow fibers (refer to SEM pictures in the following section). The shear rate has more impact to the orientation of molecular chains in the outer skin layer than to that in the inner surface because the rapid and vigorous coagulation happened in the outer surface. On the other hand, the overall mass transfer resistance is the combination of the resistances of inner and outer skins. Therefore, the existence of inner skin structure makes the overall mass transfer less sensitive to the change of shear rate.

Morphology of Hollow Fiber Membranes

The microstructures of hollow fiber membranes observed by SEM are exhibited in Figure 2. The sample was obtained from run No.1 of the batch 2, which used glycerol as the bore liquid. Pictures (a) and (b) show the cross-sections of the hollow fiber, (c) and (d) are the cross-sections of hollow fiber near inner surface and outer surface, respectively, pictures (e) and (f) depict the outer surface and the inner surface of the hollow fiber, respectively.

As shown in these pictures, no finger voids could be observed in the membrane cross-sections, and no pin holes could be found in the outer surface of the hollow fiber. In addition, there is a relatively dense skin structure on the inner surface of pictures (d) and (f). In other words, the resulted hollow fiber spun using glycerol as the bore liquid is an asymmetric membrane with dual skin structures. This might be due to phase separation occurring in the inner surface, and there is no convective flow of the bore fluid because of the high viscosity of glycerol. As a consequence, a relative dense skin layer was formed and no finger voids existed.
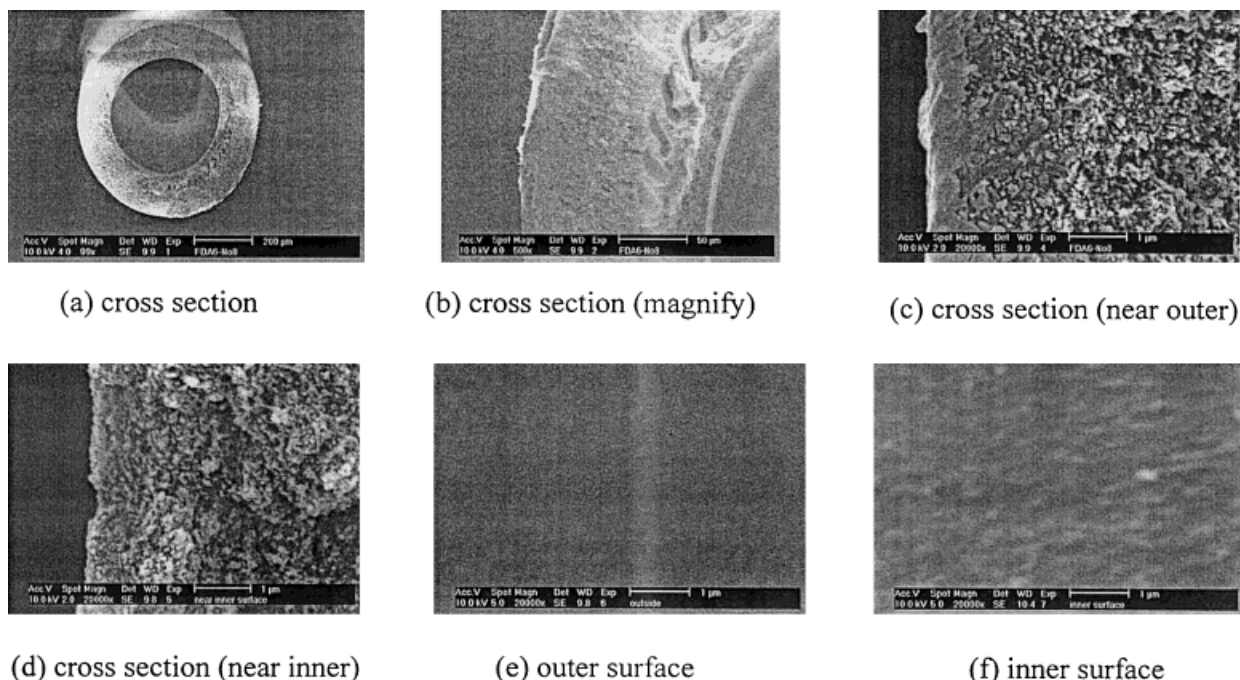
(a) cross section

(b) cross section (magnify)

(c) cross section (near outer)

(d) cross section (near inner)

(e) outer surface

(f) inner surface

Figure 3   SEM pictures of hollow fibers (run No. 8 in Table V).

The microstructures of the sample obtained from run No. 8 of the batch 2, which used the NMP/H_2O (2 : 1 weight ratio) mixture solvent as the bore liquid, are shown in Figure 3. Picture (a) shows the cross sections of the hollow fiber, the magnified cross sections are shown in (b). Pictures (c) and (d) are cross-sections of hollow fiber near inner and outer surfaces, respectively, and (e) and (f) are the outer and the inner surfaces of hollow fibers, respectively.

As indicated in picture (b), finger-like voids are observed near inner surface, possibly because the bore fluid diffused convectively into the inner surface and induced spinodal phase separation immediately. There is no visible defects on the outer surface of the hollow fiber in pictures (c) and (e). No clear dense inner skin is found from pictures (d) and (f). In other words, the hollow fiber membrane mainly possesses single outer skin dense structure, which is different from the sample when glycerol is used as the bore liquid. As a result, hollow fibers spun with NMP/H_2O (2 : 1 weight ratio) as the bore fluid may have higher permeances than those prepared with glycerol. In addition, the existing of single dense skin structure probably makes fibers spun with NMP/H_2O more sensitive to the change in shear rate than those fibers spun with glycerol.

CONCLUSIONS

Asymmetric 6FDA-durene polyimide hollow fiber membranes were spun from two *in situ* imidization dopes consisting of 14.7% of 6FDA-durene in a NMP solvent. We have investigated the effects of air gap, shear rates within a spinneret, and bore fluids on gas separation performance of these fibers. The performance of hollow fibers spun from two dopes with different viscosities was also compared. It is found that hollow fibers spun from different IV show different separation performances. A high-viscosity dope made from a high IV 6FDA-durene material is essential to yield defect-free hollow fiber membranes for gas separation.

A defect-free 6FDA-durene asymmetric hollow fiber with a selectivity of 28.8 for CO_2/N_2 and a permeance of 227.6 GPU for CO_2, and a selectivity of 4.2 for O_2/N_2 and a permeance of 33.1 GPU for O_2 have been developed by using the higher IV viscous dope. It seems that it is essential to have the spinning dope with a viscosity in the region of chain entanglement to yield hollow fibers with minimum defect.

Experimental data also demonstrate that the permeance increases greatly for the medium IV (0.64 dL/g) dope when an air gap is employed in the spinning process. This is due to the effect of

air-gap induced elongational stress on relatively mechanically weak fibers. The stress results in more defect structure of the skin selective layer.

The hollow fibers spun with NMP/H_2O as the bore liquid have higher permeances and selectivities than those spun with glycerol as the bore liquid because the former has a relatively looser inner skin structure than the latter. In addition, the selectivity of hollow fibers spun with NMP/H_2O as the bore liquid changes modestly with shear rate, while the selectivity of hollow fibers spun with glycerol as the bore liquid are less sensitive to the change of shear rate.

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