Aging Phenomenon of 6FDA–Polyimide/Polyacrylonitrile Composite Hollow Fibers

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SYNOPSIS

We have observed time-dependent drifts in permeability and selectivity for two types of composite hollow fibers used for air separation. One was PVP [poly(4-vinyl pyridine)]/6FDA–durene/polyacrylonitrile (PAN) composite hollow fiber, and the other was 6FDA–3,5-diaminobenzonitrile/6FDA–durene/PAN composite hollow fiber. Their permeabilities dropped 50 to 70% after 3 to 5 months, while selectivities for O_2/N_2 deteriorated slightly with time. A systematic study was carried out to investigate the causes of this creep behavior. Various composite fibers, such as polyimide/Celgard and polyimide siloxane/PAN, were fabricated to simulate the aging process. We conclude that the aging phenomenon observed for these two 6FDA–durene/PAN composite fibers was not due to the structure change of the PAN substrate, but mainly to the densification effect of the 6FDA–durene gutter layer on composite fibers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Microporous composite membranes consisting at least of a thin selective layer backed by a microporous substrate have received a lot of attention recently.[1-9] This is because the fabrication of an asymmetric membrane is not cost effective if an expensive polymer is used, and it is sometimes difficult to form a useful asymmetric membrane from a brittle polymer. One must adopt the multilayer microporous composite concept to fabricate membranes in order to reduce material quantities and costs. As a result, both industry and academia have spent considerable effort on developing new-generation air separation membranes based on the microporous composite concept.

A composite membrane usually has three layers, an ultrathin skin layer (thickness < 1000 Å), a gutter layer, and a porous substrate, as illustrated in Figure 1. The substrate has a structure either asymmetric or symmetric, but its surface may be full of submicron pores or have a thin dense layer. The main purposes of this support layer are (1) to lower material cost, and (2) to provide membranes with reasonable mechanical properties.[7-14] Using a microporous substrate can eliminate substantial substructure resistance to gas transport. The gutter layer is an intermediate layer in a composite membrane and is usually made of a highly permeable material. It has multiple functions; for example, it enhances the adhesion between the top layer and the substrate and increases the permeance through a multilayer structure. Sometimes the gutter layer can be eliminated if the substrate is highly permeable and if the adhesion between the top layer and the substrate is good. The top layer is usually made of a material with a high selectivity. Many composite membrane systems have been reported. For example, Kimmerle et al.[1] and Gudernatsch et al.[2] developed microporous composite membranes from poly(dimethyl siloxane) (PDMS) or poly(butadiene styrene) (BS)/microporous poly(ether sulfone) (PES) systems. Cabasso and Tamvakis developed polyethyleneimine/PS hollow fibers.[3] Bikson et al. at Union Carbide extended and modified Cabasso and Tamvakis's approach and developed various composite membranes for $H_2/$

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Journal of Applied Polymer Science, Vol. 59, 77–82 (1996)
 CCC 0021-8995/96/010077-06

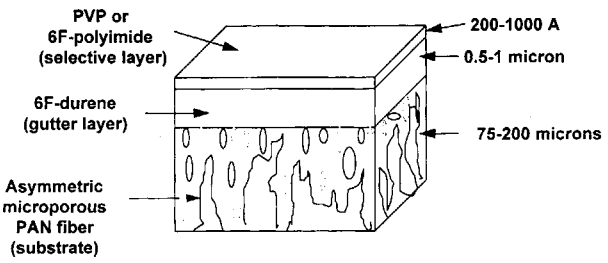

Figure 1 A typical three-layer composite membrane structure.

N_2 separation.[4] Air Products employed poly[1-trimethyl(silyl)-1-propyne] (TMSP) to form microporous composite membranes.[5] Du Pont researchers developed a bilayer hollow fiber with an asymmetric outer layer.[7] The Koros group worked on polyimide/ceramic and polycarbonate/ceramic composite membranes.[8] Chung and his co-workers at Hoechst Celanese developed composite hollow fibers for air separation from 4-PVP [poly(4-vinyl pyridine)]/6FDA (hexafluoropropane dianhydride)-durene/PAN and from 6FDA-DBN (3,5-diaminobenzonitrile)/6FDA-durene/PAN.[9] Figure 1 shows their three-layer membrane structure. Development of other composite fibers with an ultrathin selective layer has also been patented by Gochanour[10] and Haubs and Hassinger[11] on microporous substrates. Various mathematical models for the gas diffusion through these membranes have been developed.[9,12-14]

In this article we continue our previous work on 4-PVP/6FDA-durene/polyacrylonitrile (PAN) and 6FDA-DBN/6FDA-durene/PAN composite hollow fibers[9] and report their separation performance as a function of time. Both fibers had excellent separation performance in the early stage, but their performance deteriorated significantly with time. A similar creep phenomenon has been reported elsewhere[8,15,16] and has been summarized by Koros and Chern[17] and Rezac et al.[8] It appears that the aging phenomenon is more profound in composite membranes than in asymetric ones. There are two explanations for this creep behavior: (1) the compaction or deformation of substructure, and (2) the glassy-state drifts in one of the multilayers. The former may reduce pore sizes and induce extra resistance for air transportation, while the latter will reduce free volume and permeability. To pinpoint the causes of this aging phenomenon in our systems, a systematic analysis was carried out in this work to characterize and understand the creep behavior of permeance for various composite fibers.

EXPERIMENTS

PVP/6FDA-Durene/PAN and 6FDA-DBN/6FDA-Durene/PAN Composite Hollow Fibers

Both fibers were prepared according to the procedure described in the previous article.[9] Microporous PAN fibers were dry-jet wet spun from a 24 wt % PAN dope in *N*-methyl-pyrrolidone (NMP) using water as the external coagulant and 95/5 NMP/water as the bore fluid. The external surface pore size is about 150 to 200 Å, with a fully porous internal surface structure. The gutter layer material, 6FDA-durene polyimide, was synthesized from hexafluoro propane dianhydride (6FDA) and durene diamine, as described in previous literature.[18,19] Its oxygen permeability was 72 barrers, and α for O_2/N_2 was 4.3 at 25°C. The deposition of a thin 6FDA-durene layer on a PAN fiber was carried out by prewetting the PAN fiber with Fluorinert® from 3M. The prewetting can prevent the 6FDA-durene/chloroform solution from penetrating PAN fibers. The deposition of a thin 4-PVP or 6FDA-DBN selective layer on dry 6FDA-durene/PAN fibers was carried out by solution coating. The deposited thickness was 277 Å for 4-PVP and 340 Å for 6FDA-DBN. 4-PVP has been known to be a good barrier material, but its true properties are not available in the literature because it cannot be formed into a free-standing film. The 6FDA-DBN polyimide was synthesized from 6FDA and 3,5-diaminobenzonitrile. Its oxygen permeability was 3.25 barrers, and α for O_2/N_2 was about 7.15 at 24°C.

Tests

Five-filament glass modules 14 cm in length were fabricated to test PAN fiber performance. Since the PAN substrate is a microporous membrane, one can measure gas flow rates at a specific pressure and O_2/N_2 selectivity if Knudsen diffusion occurs. For composite fibers, the modules were 20 cm long with an inside diameter (i.d.), of 1.5 cm. Each module consisted of 25 to 100 filaments. For both 14-cm- and 20-cm-long glass modules, gas flow tests were carried out by applying pressure from the shell side, and the permeances were measured from the bore. The test temperature was 25°C. The selectivity, α, for gas a to gas b is defined as

$$\alpha = \frac{(\frac{P}{L})_a}{(\frac{P}{L})_b} \quad (1)$$

Table I 0.7% PVP/0.2% 6FDA–Durene PAN Fiber Performance

Time (days)	α O_2/N_2	O_2 Permeance (GPU*)
2	5.6	32.2
7	5.5	30.7
16	5.7	28.2
25	5.1	20.1
52	5.0	14.5
62	5.1	13.3
121	4.6	13.3

Twenty-five filaments were tested at 139.7 kPa (20 Psi).
* 1 GPU unit = 10^{-6} cc(STP)/cm^2 s cm Hg.

where P/L is the permeance for gas a or gas b. The test temperature was about 25°C, and the test pressure varied from 14 kPa to 350 kPa (from 2 psi to 50 psi).

Mechanical Properties

Tensile properties of PAN hollow fibers were measured at an 8.46-cm (3.33-inch) gauge length with a speed of 5.08 cm/min using an Instron test unit. The test method was based on ASTM procedure.

RESULTS AND DISCUSSION

Aging Phenomenon of PVP/6FDA–Durene/PAN and 6FDA–DBN/6FDA–Durene/PAN Composite Hollow Fibers

As shown in Tables I and II, the permeances of these two composite fibers decayed significantly with aging, while their selectivity remained almost the same

Table II 0.5% 6FDA–DBN/2% 6FDA–Durene/PAN Fiber Performance

Time (days)	α O_2/N_2	O_2 Permeance (GPU*)
2	5.1	37.2
7	5.0	34.7
16	5.1	32.1
42	4.8	19.6
50	5.1	14.9
62	4.9	13.4
121	4.8	13.9

One hundred filaments were tested at 139.7 kPa.
* 1 GPU unit = 10^{-6} cc(STP)/cm^2 s cm Hg.

Table III Microporous PAN Fiber Properties

Time (days)	α O_2/N_2	O_2 Flow Rate (cc/min)
2	0.91	172
7		170
9		169
15	0.91	170
28	0.91	172
51	0.91	169
86	0.91	168

Five 13.5-cm filaments tested at 14 kPa (2 psi).

in the early stage of testing and then gradually dropped with time. Similar results were reported by Rezac et al. on polyimide/ceramic and polycarbonate/ceramic composite membranes.[5] They observed a 40 to 60% reduction in gas flux for both membranes in 20 days; however, the membranes' O_2/N_2 selectivities increased slightly with time.

Originally, we thought that this decay might be due to the nature of PVP, so we replaced it with 6FDA–DBN. However, 6FDA–DBN/6FDA–durene/PAN composite hollow fibers also decayed with time. Therefore, the reduction of permeance was not likely to have been caused by the selective layer. To identify the causes for the permeance drop, other experiments were carried out to investigate the aging phenomena of microporous PAN substrates and 6FDA–durene/PAN composite fibers.

Table III exhibits the results for PAN fibers and indicates that their separation performance and air flow rates remains almost unchanged during a three- to four-month period. This information implies that there is no significant change in their porous struc-

Table IV Mechanical Properties of PAN Hollow Fibers

Time (days)	Initial Modulus (g/d)	Tensile Strength (g/d)	Maximum Elongation (%)
1	14.3	0.27	3.4
8	14.8	0.28	3.9
15	14.6	0.27	3.3
22	14.9	0.27	3.7
31	14.6	0.29	4.5
62	15.0	0.28	3.1
92	15.1	0.28	3.5
121	14.5	0.28	4.5

Note: 1 g/d × 8.83 = cN/tex.

Table V 2% 6FDA–Durene/PAN Fiber Performance

Time (days)	α O_2/N_2	O_2 Permeance (GPU*)
2	4.0	70.4
23	3.6	39.3
37	3.7	32.2
116	3.7	29.2

One hundred filaments were tested at 139.7 kPa.

Table VI 1% 6FDA–Durene/PAN Fiber Performance

Time (days)	α O_2/N_2	O_2 Permeance (GPU*)
2	3.2	132.7
7	3.4	116.7
11	3.3	98.6
18	3.5	93.1
23	3.4	74.5
61	3.7	67.9
96	3.4	62.3
111	3.2	56.8
136	3.4	55.8

One hundred filaments were tested at 139.7 kPa.
* 1 GPU unit = 10^{-6} cc(STP)/cm^2 s cm Hg.

ture. Table IV summarizes PAN fiber mechanical properties as a function of time and shows no remarkable change in PAN mechanical properties. As a result, the structure change of PAN fibers with time seems to be negligible. Table V reports the time-dependent drifts in permeance and selectivity for a 2% 6FDA–durene/PAN composite fiber. The 2% in front of 6FDA–durene means that this composite fiber was prepared by solution coating a PAN fiber with a 2 wt % 6FDA–durene solution. The 6FDA–durene coating layer had a thickness of 9900 Å. Its permeances dropped 60 to 70% after three to four months, and these results were in agreement with what we observed in Tables I and II. Table VI gives the separation performance for a 1% 6FDA–durene/PAN fiber with a coating thickness of 2500 Å. Figures 2 and 3 illustrate its permeance shift as a function of time in regular and semilog plots. Permeance decayed rapidly in the early stage of aging (about 20 days) and then continued a slow creep, while its selectivity stayed almost the same over the entire test period. A similar phenomenon, but with a much smaller permeance decay, was reported by Mazur and Chan on cellulose acetate.[15]

Does 6FDA–durene densify with aging? We retested a 15-month-old module made from wholly asymmetric 6FDA–durene fibers.[18] Table VII shows the results; the permeance did drop about 40% after 15 months with a slight increase in α. Was this permeance reduction caused by the chemistry of a substrate? Was PAN able to induce 6FDA–durene densification? Extra experiments were conducted by M. Spak and showed that a 6FDA–durene/Celgard (polypropylene) fiber also reduced 40% in 3 months (Table VIII). Based on these results, we believe that the permeance reduction in the current systems was mainly due to the densification of 6FDA–durene material. In other words, although 6FDA–durene is a highly permeable polyimide, it is a glassy polymer,

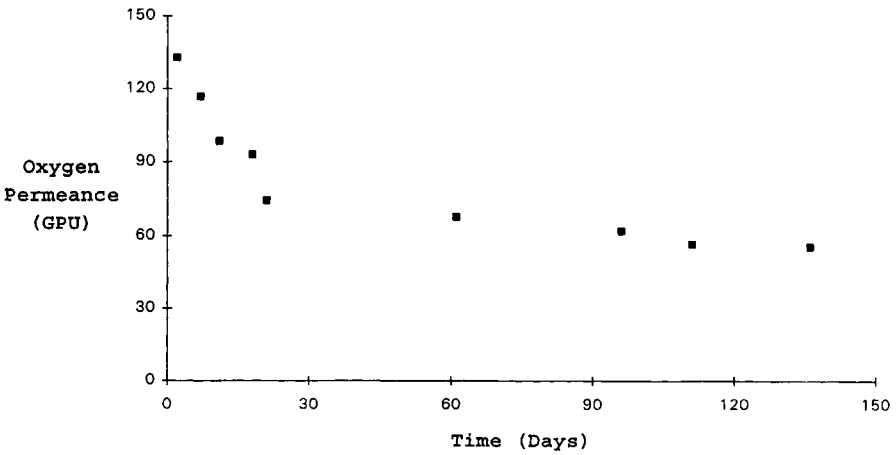

Figure 2 Aging phenomenon of 1% 6FDA-durene/PAN composite fiber.

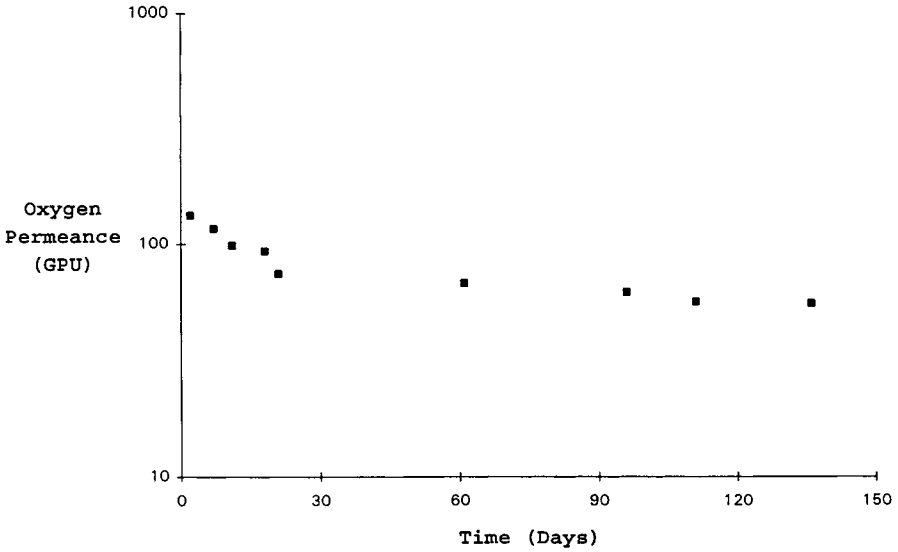

Figure 3 Semilog plot of aging phenomenon of 1% 6FDA-durene/PAN composite fiber.

and its free volume reduces with age. To confirm our conclusion, a silicone polyimide/PAN fiber was prepared. This silicone polyimide, synthesized by Dr. R. Sandor, has an O_2 permeance of 400 barrers with an α of 2.0 at room temperature. Table IX gives its separation performance as a function of time and shows that its permeance dropped only slightly with time. This was because silicone polyimide was a rubber-like material, and its free volume usually did not change significantly with time. We have thus concluded that the permeance reduction in the current systems was mainly due to the densification of 6FDA-durene material.

How does one explain the deterioration of composite fiber selectivities as shown in Tables I and II? This was probably due to the detrimental effect of 6FDA-durene densification on the extra-thin PVP and 6FDA-DBN layers. Based on the molecular modeling, 6FDA-durene has a free volume of 29% (as free volume is defined by Koros[14]). The calculated free volume changes to 27.5% if the permeance drops from 72 barrers to 40 barrers.[20] As a result, a 45% drop in permeance may indicate that 6FDA-durene experiences a volume shrinkage of 1.5%. Since the thicknesses of PVP and 6FDA-DBN layers were 277 and 340 Å, respectively, they prob-

Table VII Aging Phenomenon of Wholly Asymmetric 6FDA-Durene Fibers

Time (days)	α O_2/N_2	O_2 Permeance (GPU*)
1	5.0	188.4
488	5.2	109.6

Five 13.5-cm filaments module.
* 1 GPU unit = 10^{-6} cc(STP)/cm^2 s cm Hg.

Table VIII 6FDA-Durene/Celgard Fiber Performance

Days	α O_2/N_2	O_2 Permeance (GPU*)
1	4.6	10.4
74	~5	6.3

Two hundred filaments were tested at 139.7 kPa.
* 1 GPU unit = 10^{-6} cc(STP)/cm^2 s cm Hg.

Table IX Silicone Polyimide/PAN Fiber Performance

Days	α O_2/N_2	O_2 Permeance (GPU*)
2	1.74	382.3
10	1.77	370.2
15	1.75	362.2
28	1.76	364.2
52	1.81	350.1
71	1.76	358.2
93	1.76	358.2
108	1.81	356.1

One hundred filaments were tested at 139.7 kPa.
* 1 GPU unit = 10^{-6} cc(STP)/cm^2 s cm Hg.

ably cracked because they did not have sufficient strength to withstand the stress created by the 6FDA–durene layer during the densification process. PVP was much more brittle than 6FDA–DBN. Therefore, as shown in Tables I and II, a composite fiber made from PVP lost its α more than that made from 6FDA–DBN. The selectivity deterioration was not observed by Rezac et al. because their composite membranes only had two layers.[8]

CONCLUSION

In this article we have investigated the effect of aging on membrane performance and identified the cause for creep behavior. For a microporous composite hollow fiber membrane using a highly permeable and glassy material as the gutter layer, the time-dependent shifts on separation performance are a critical issue. The permeance may decrease significantly in the early stage of aging and then decrease more slowly, while its selectivity stays almost the same in the early stage and then deteriorates. We believe that this reduction in separation performance is mainly due to the effects of the gutter-layer densification.

The authors thank W. M. Cooper, R. Sandor, P. Foley, S. Jacobson, and M. Spak for providing them with helpful information and comments.

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Received November 30, 1994
Accepted May 23, 1995