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Standardization in the Production and Testing Procedures for Polyethersulfone Hollow Fiber Ultrafiltration Membranes

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ABSTRACT

Several hollow fiber ultrafiltration membranes have been produced from polyethersulfone–polyvinyl pyrrolidone–*N*-methyl-2-pyrrolidone solutions and tested. The effects of feed flow velocity through the fiber bore on pressure drop in the test fiber bundle, membrane separations for PEG solutes, and the obtainable mass transfer coefficients under the test conditions have been experimentally determined and discussed. Further, the effects of storage time and prefiltration of the fiber casting polymer solution on the performance characteristics of the resulting membranes have been studied. The viscosity of the fiber casting solution increased upon storage for a few weeks, and it decreased after the solution was filtered prior to use in fiber production. Storage time and filtration treatment of the fiber casting solution had significant effects on the morphology of the resulting membranes. Casting solution of longer storage time and without filtration pretreatment produced smaller size pores on the membrane bore-side skin layer, and a larger number of such pores and/or a thinner skin layer in the resulting membrane. On the basis of these results, the need for standardizing the fiber producing conditions and fiber testing procedure is pointed out, and a few suggestions are made for such standardization.

INTRODUCTION

Polymeric hollow fiber (HF) membranes offer two major advantages over flat sheet or tubular membranes, namely, they have far more mem-

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brane area per unit volume, and hence higher productivity per unit volume of membrane module, and in addition, they are self-supporting. The HF configuration is therefore currently the preferred choice for membrane modules in separation applications. Polymeric HF membranes, with or without surface modifications, are especially versatile in utility for a wide variety of low pressure applications such as those involved in ultrafiltration (UF), microfiltration (MF), pervaparation, and gas–vapor (and also some gas–gas) separations. The large increase in technology development work on the production of HF membranes reported in recent literature (1–6) is a clear recognition of this versatility in many industrial applications.

There are several experimental variables in the usual method of producing and testing HF membranes. For example, in the laboratory technique illustrated in the work of Liu et al. (2), variables such as composition and temperature of the fiber casting polymer solution, nature of the internal coagulant and its flow rate, length of air gap, the extrusion pressure used for fiber spinning, as well as details of spinnerette design were considered. In order to establish cause–effect relationships among these variables with respect to UF performance of the resulting fibers, experimental procedures involved in the production and testing of HF need to be standardized with respect to each variable, in as much detail as possible, for purposes of comparison of data on fiber performance. The object of this paper is to call attention to a few aspects of such standardization.

The first aspect is with respect to the structure of the polymer solution used for fiber production. In this context, the term ''solution-structure'' refers to the state of aggregation and disposition of polymer segments within the fiber casting solution. While the importance of such ''solution-structure'' to the performance characteristics of the resulting membranes has been pointed out in the literature (7), no single physicochemical parameter has been identified to characterize solution structure completely. In practice, this means that even though the overall composition and temperature of the fiber casting polymer solution may appear unchanged, the performance characteristics of the resulting fibers produced under otherwise identical experimental conditions could be significantly different because of possible differences in the conformational structure of the polymer in the solution used. Polymer conformational structure is governed not only by the overall composition and temperature of the polymer solution, but also by other factors involved in its preparation such as method of mixing and storage time. Since the latter details are not usually strictly controlled and documented in the literature, comparison of fiber performance data becomes difficult, and may even be misleading.

The second aspect is with respect to the fiber testing procedure for performance characterization. Again, in the laboratory technique of the type illustrated in the work of Liu et al. (2), the fibers are tested for solute separation and permeate fluid flux characteristics by pumping dilute aqueous solutions of polyethylene glycol (PEG) of different molecular weights through the capillary bore of the fibers under specified experimental conditions of operating pressure and feed flow rate. The results on PEG separation (%) and membrane permeated product rate (PR, in g/$cm^2 \cdot h$) are reported to characterize the fibers tested. As to pressure drop between the inlet and outlet points and actual feed flow rates used for each fiber during testing, such important data are often lacking or ambiguous in the literature. Depending on the experimental conditions used for fiber production, fibers of different physical dimensions [outside diameter (o.d.), inside diameter (i.d.), and wall thickness] are obtained. For example, Miao had shown (8) that more than twofold variations in o.d. and i.d. in the resulting fibers were possible through the same spinnerette, depending on the experimental conditions of fiber production. For a given inlet pressure and volumetric feed flow rate used during fiber testing, the outlet pressure and the fluid velocity through the fiber bore will be different for each fiber length and fiber i.d. in the bundle, which will significantly affect performance characteristics of the different fibers tested. Consequently, standardization with respect to the above variables during fiber testing is necessary for a meaningful comparison of performance data of the different fibers produced.

Attention is thus focused on the above two aspects of standardization in this report.

EXPERIMENTAL

Materials

Polyethersulfone (PES, Victrix 4800), supplied by Imperial Chemical Industries, was dried for 3 hours at 150°C and used as membrane material without further purification. *N*-Methyl-2-pyrrolidone (NMP), supplied by Merck, and polyvinylpyrrolidone (PVP) of molecular weight 10,000, supplied by Sigma Chemical Co. were used as solvent and additive, respectively, in the preparation of the fiber casting solution. Poly(ethylene glycols) (PEG) of different molecular weights, supplied by Aldrich Chemical Co. and Merck, were used as reference solutes for characterizing fiber performance.

Fiber Casting Solutions

Three fiber casting solutions were used in this work (see Table 1).

It may be noted that an NMP/PVP ratio of 7 was held constant for all three solutions. The components were mixed in a 1-L glass bottle which

TABLE 1
Fiber Casting Solutions

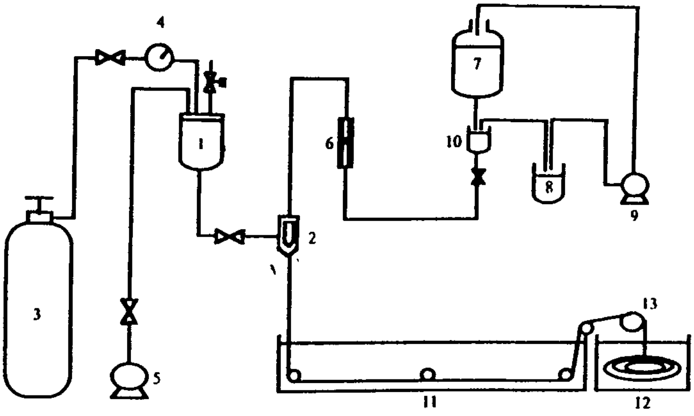
Solution	PES (wt%)	NMP (wt%)	PVP (wt%)
M1	20	70	10
M2	22	68.25	9.75
M3	24	66.5	9.5

was roller-mixed for 2 hours every day for 9 consecutive days and kept in an oven at 60°C except during mixing. The polymer solution so obtained, unless otherwise stated, was used for fiber spinning. For some experiments the polymer solution was kept under storage at room temperature (23 ± 1°C) for a specified period (1 to 5 weeks) with roller-mixing for 2 hours every day before use.

Fiber Spinning and Fiber Characterization

All experiments were carried out at laboratory temperature (~24°C). The polymer solution was usually filtered (unless stated otherwise) under 5–10 psig nitrogen pressure using a 200-mesh filter disk together with a polyester fabric. After filtration, the spinning solution was transferred into a solution tank in the fiber spinning system (Fig. 1). The tank was subsequently evacuated for 20 minutes to let entrapped gas bubbles escape. The solution was then kept in the tank under nitrogen for at least 2 hours (for any residual gas bubbles to escape) before use in the fiber spinning operation. The apparatus, fiber spinning procedure, and the fiber testing technique used were essentially the same as those reported in the literature (2).

The spinnerette had a tube-in-orifice design as shown in Fig. 2 (2). The polymer solution entered the side opening of the spinnerette under an extrusion pressure (EP, psig) of nitrogen; simultaneously, the internal coagulant (in this case, deionized water at room temperature) entered the central tube of the spinnerette at a preset flow rate (water flow rate, WFR, mL/min). The nascent fiber, partially coagulated by water, passed through a length of air gap (LAG, cm), and then entered the external coagulant bath of deionized water at ~2°C. When LAG was changed, the internal water flow rate was adjusted to keep the WFR reading constant at the preset value. The coagulation process was completed in the external water bath, and the hollow fiber membrane produced. The membranes so produced were kept under water for at least a week (to leach out the residual water-soluble solvent and additive) before they were tested for their physical dimensions and ultrafiltration (UF) performance characteristics.



1. Polymer Solution Tank
2. Spinnerette
3. Nitrogen Cylinder
4. Pressure Gauge
5. Vacuum Pump
6. Rotameter
7. Internal Coagulant Tank
8. Overflow Tank
9. Pump
10. Funnel
11,12. External Coagulant Bath
13. Spooling Machine

FIG. 1 Schematic diagram of the apparatus for hollow fiber spinning.

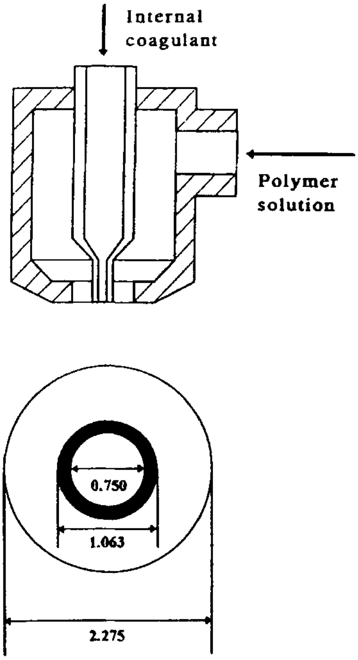


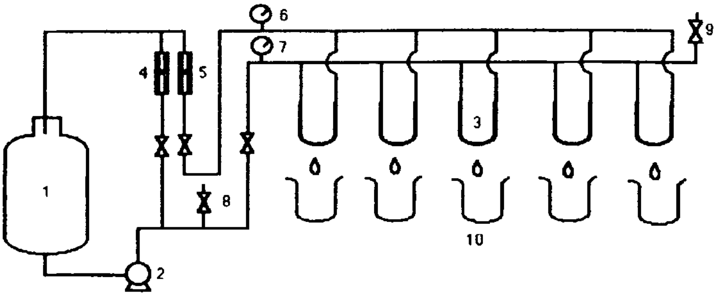
FIG. 2 (Top): Schematic diagram of the spinnerette assembly. (Bottom): Schematic diagram of cross section of the spinnerette used (units in mm).

Under these experimental conditions, HF with asymmetrically porous fiber walls having a solute rejecting skin layer on the inside (bore side) wall surface, were produced. Asymmetricity of porous structure was confirmed by SEM (scanning electron microscope) (8).

During the fiber spinning process, the nascent fiber velocity (NFV, cm/s) was determined by collecting a sample of well-coagulated fiber of known length produced within a known time interval from the external coagulation bath.

In addition, for a particular spinnerette design and fiber spinning conditions used, the values of polymer solution flow velocity (V_P, cm/min), and water (internal coagulant) flow velocity (V_W, cm/min) were also determined for each fiber produced. The quantity V_P is the volumetric flow rate of the polymer solution divided by the effective cross-sectional area available for solution flow at the spinnerette exit. Similarly, the quantity V_W is the volumetric flow rate of water (internal coagulant) divided by the effective cross-sectional area available for water flow at the spinnerette exit. The physical dimensions of the HF produced (o.d., mm; i.d., mm; and wall thickness, mm) were determined in each case using a stereomicroscope.

The experimental apparatus used for UF performance characterization of the HF is shown in Fig. 3 (2). In this work, the HF bundles were made as follows. Six pieces of HF, each 26 cm long were collected into a bundle. The external surfaces at the two bundle ends were then covered with



1.	Solution Tank	6.	Outlet Pressure Gauge
2.	Pump	7.	Inlet Pressure Gauge
3.	Membrane Bundles	8,9.	Safety Release Valves
4,5.	Rotameters	10.	Collecting Containers

FIG. 3 Schematic diagram of hollow fiber membrane test system.

epoxy glue. Each end was potted into a ¼-inch diameter polypropylene tube of 3 cm length. The glue was then allowed to set at normal laboratory environment for at least 3 hours while keeping the unpotted parts of the fibers under water. The potted bundle was then assembled into the test apparatus. For test purposes, the feed fluid was pumped through the fiber bore, and fluid permeation through the membrane was from inside to the outside fiber wall.

TABLE 2

Details of Fibers Produced and Characterized[a,b]

No.	1	2	5	7	8	9
Fibers	M1-0-10-80-5	M1-0-5-80-5	M1-1-10-80-5	M1-3-5-80-5	M1-5-10-80-5	M1-5-5-80-5
Storage (weeks)	0	0	1	3	5	5
Viscosity (m·Pa·s)	2314	2314	2710	2605	2103	2103
Composition	M1	M1	M1	M1	M1	M1
WFR (mL/min)	10	5	10	5	10	5
LAG (cm)	80	80	80	80	80	80
EP (psig)	5	5	5	5	5	5
o.d. (mm)	1.1175	0.979	1.185	1.0786	1.1875	1.1125
i.d. (mm)	0.8875	0.70	0.9125	0.6411	0.9625	0.83
Thickness (mm)	0.12	0.14	0.14	0.22	0.11	0.14
o.d./i.d.	1.26	1.40	1.30	1.68	1.23	1.34
NFV (cm/s)	16.16	11.19	12.71	ND	14.25	10.49
V_P (cm/min)	ND	ND	139.90	144.20	114.80	114.80
V_W (cm/min)	2273	1136	2273	1136	2273	1136
V_W/V_P	ND	ND	16.25	7.88	19.80	9.90
Average PR ($g/cm^2{\cdot}h$)	10.48	5.32	5.43	3.69	9.05	4.29

No.	10	11	12	13	14	17
Fibers	M1-5-5-50-5	M1-5A-5-50-5[c]	M1-5A-5-80-5[c]	M1-5A-10-80-5[c]	M2-5-80-5	M3-5-80-5
Storage (weeks)	5	5	5	5	0	0
Viscosity (m·Pa·s)	2103	2851	2851	2851	3590	7744
Composition	M1	M1	M1	M1	M2	M3
WFR (mL/min)	5	5	5	10	5	5
LAG (cm)	50	50	80	80	80	80
EP (psig)	5	5	5	5	5	5
o.d. (mm)	1.2781	1.18	1.082	1.1317	1.0804	1.0733
i.d. (mm)	0.9438	0.86	0.756	0.945	0.8321	0.89
Thickness (mm)	0.17	0.16	0.16	0.09	0.12	0.09
o.d./i.d.	1.35	1.37	1.43	1.20	1.30	1.21
NFV (cm/s)	9.40	9.35	ND	15.35	7.62	6.93
V_P (cm/min)	114.79	64.69	64.69	64.69	56.26	40.57
V_W (cm/min)	1136	1136	1136	2273	1136	1136
V_W/V_P	9.90	17.57	17.57	35.13	20.20	28.01
Average PR ($g/cm^2{\cdot}h$)	5.28	4.99	4.58	7.13	5.45	5.95

[a] Composition: M1 (PES/PVP/NMP) = 20/10/70; M2 (PES/PVP/NMP) = 22/9.75/68.25; M3 (PES/PVP/NMP) = 24/9.5/66.5.

[b] ND = not determined.

[c] Unfiltered fiber casting solution.

UF performance of the fibers was characterized by their PWP (pure water permeation rate, g/cm^2·h), PR (membrane permeated product rate, g/cm^2·h), and UF separation (%) for PEG solutes of different molecular weights at the average operating pressure of 20 psig and at a feed flow velocity of 1.8 to 2.0 m/s (unless stated otherwise). The PEG concentration in the feed solution was 200 ppm. Solute concentrations in the feed and in the product solutions were determined using a Shimadzu Total Carbon Analyzer Model 5000. The percent solute separation (f) was calculated from the relation

$$f = [(\text{solute ppm in feed} - \text{solute ppm in product})/\text{solute ppm in feed}] \times 100\%$$

Because of the very low solute concentrations involved, PWP and PR data were essentially the same in all the experiments carried out; hence, only PR data are reported here. These data were obtained by weighing permeate samples collected in a preset period of time, which were then converted into grams per unit effective inside fiber surface area in the bundle per unit time (g/cm^2·h). The experimental data obtained with different fibers are given in Table 2 where each fiber is designated by the composition of its fiber casting solution (M1, M2, or M3), followed by four numbers indicating storage time (weeks), WFR (mL/min), LAG (cm), and EP (psig), respectively.

RESULTS AND DISCUSSION

Effect of Feed Velocity on Pressure Drop

Figure 4 shows a typical set of data on the pressure drop (psi) observed as a function of feed solution velocity through a fiber bundle at a constant average operating pressure of 20 psig. The data show that beyond a certain feed velocity (0.45 m/s for the particular fiber bundle tested), pressure drop increased with an increase in feed velocity, and the correlation was linear in the range of feed velocities tested. On the basis of such data, the inlet pressure used for testing each fiber bundle was always adjusted so that the average pressure [i.e., (inlet pressure + outlet pressure)/2] always remained 20 psig. Under such test conditions the local rate of the membrane permeated product solution will be nonuniform along the length of each fiber. Hence, for purpose of comparison of data on fiber performance, the length of a test fiber was kept constant (26 cm in this work) in all the experiments reported in this work. For standardization of the fiber testing procedure, it is important to specify both the length of each test fiber and the pressure drop involved in the test fiber bundle.

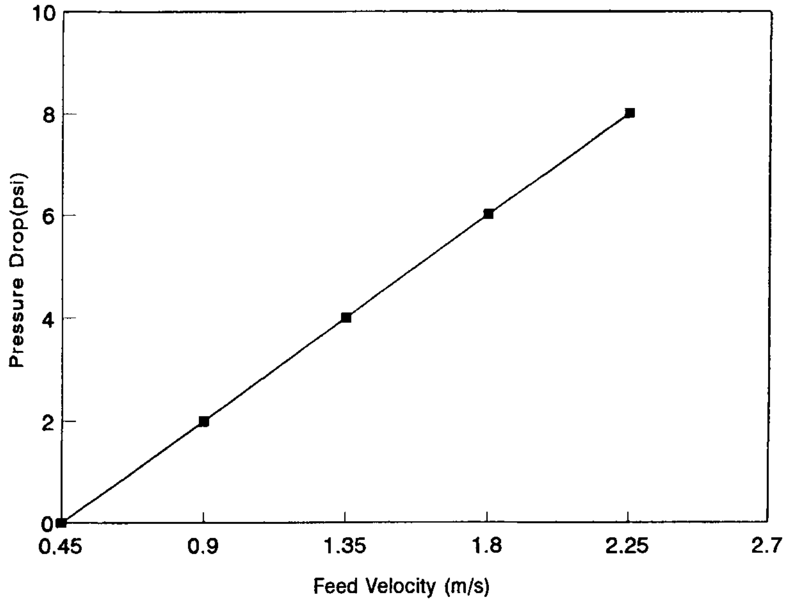


FIG. 4 Effect of feed velocity on pressure drop (average operating pressure = 20 psig).

Effect of Feed Velocity on PEG Separations

Figure 5 illustrates the effect of feed solution velocity through the fiber bore on PEG separations obtained with Fiber 1 under the average operating pressure of 20 psig. The conditions of production and other details of Fiber 1 are given in Table 2. The PEG solutes used had molecular weights in the 600 to 10,000 range, and the feed velocities in the range 0.45 to 1.8 m/s for each PEG solute. For PEG-6000, the test was also conducted at a feed velocity of 2.25 m/s. The results showed that changes in feed velocity in the 0.45 to 1.8 m/s range had a profound effect on the corresponding PEG separations. For example, the separation for PEG-6000 increased from 48 to 78% with an increase in feed velocity from 0.45 to 1.8 m/s; further increase in feed velocity did not change PEG separation significantly. Since the solute concentration in the feed solution was very small in all cases, PR values were not affected by the change in feed velocity. The above results indicate that for comparison of fiber performance data, feed velocity should be kept constant under the test conditions, and it is preferable to keep the feed velocity constant at 1.8 m/s or higher for all the tests.

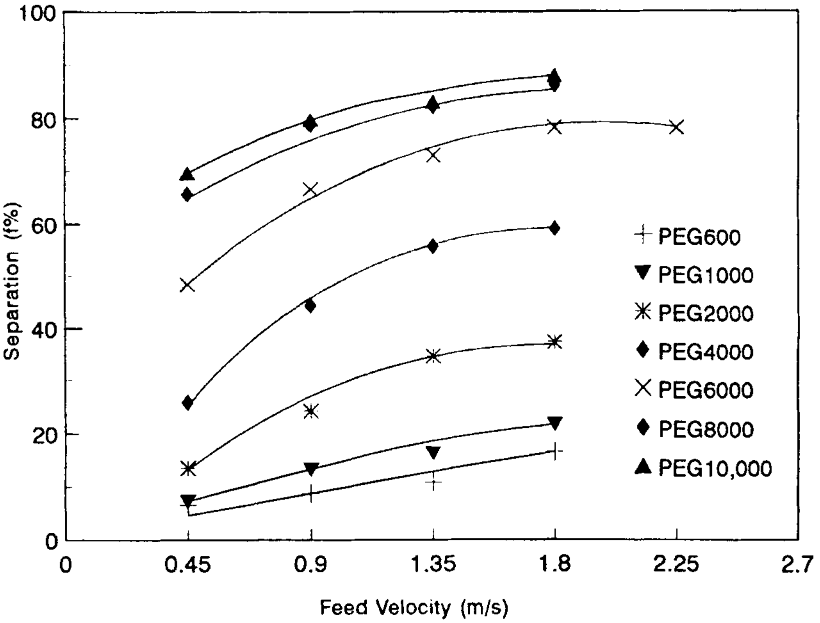


FIG. 5 Effect of feed velocity on solute separation.

Mass Transfer Coefficients Obtainable in Hollow Fiber Membranes for UF Separations

Data on mass transfer coefficients (k) are of practical interest in the applications of HF membranes for UF separations (1). At low operating pressures (P) and for very dilute aqueous PEG feed solutions, the fluid permeation velocity (V_S) through the membrane pores is proportional to P, and the solute transport parameter for each PEG solute may be assumed to be constant for each membrane. For such cases it has been shown (9, 10) that solute separation (f) will increase with increase in V_S (i.e., increase in operating pressure) when (V_S/k) < 1; f will decrease with an increase in V_S when (V_S/k) > 1, and f will pass through a maximum when (V_S/k) $=$ 1. The above theoretical considerations offer a technique for determining k values of HF membranes for UF separation (1).

Figure 6 illustrates a set of data obtained with Fiber 1 on separations of PEG-600, – 1000, and – 2000 solutes as a function of operating pressure expressed as V_S (fluid permeation velocity). In all cases the feed velocity through the fiber bore was kept constant at 1.35 m/s. The results showed that with respect to PEG-600 solute, f increased with an increase in V_S;

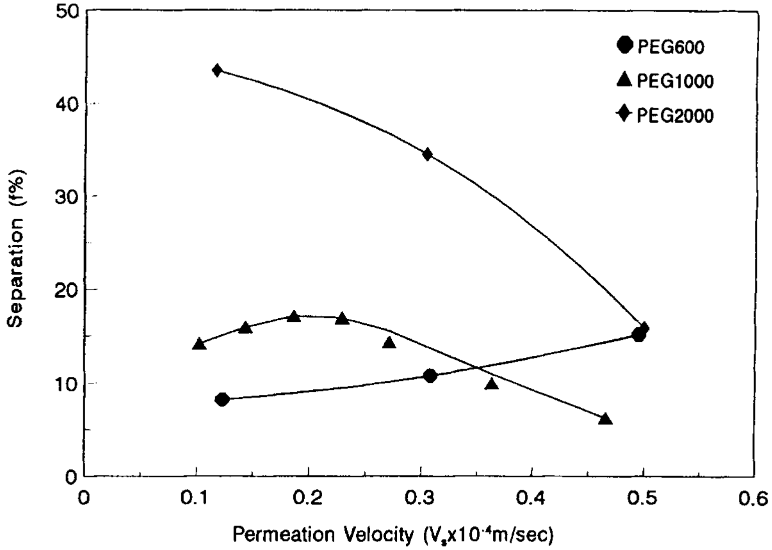


FIG. 6 Effect of permeation velocity on solute separation (feed velocity kept constant at 1.35 m/s).

with respect to PEG-2000 solute, f decreased with increase in V_S; and with respect to PEG-1000 solute, f passed through a maximum at $V_S = 0.2 \times 10^{-4}$ m/s, which means $k = 0.2 \times 10^{-4}$ m/s for PEG-1000 at a feed velocity of 1.35 m/s for the fiber studied. Since the diffusivities (D_{AB}) of PEG-600 and PEG-2000 are higher and lower, respectively, compared to D_{AB} of PEG-1000 (7), the trends observed for the separations of PEG-600 and PEG-2000 are consistent with the predictions based on the k value for PEG-1000. Further, since $k \propto (D_{AB})^{2/3}$ for dilute solutions, the k value for different solutes can be calculated from the k value for PEG-1000 at the same feed flow velocity of 1.35 m/s. Similar data can also be generated for other feed flow velocities. Therefore, from the point of view of fiber characterization, it is also preferable to experimentally determine and report the obtainable k values as a function of feed flow velocity for a reference dilute solution system such as aqueous PEG-1000.

Effect of Storage Time and Filtration Treatment of the Fiber Casting Solution on the Characteristics of the Resulting Fibers

As pointed out earlier, no single physicochemical parameter has been identified to characterize the structure of a polymer membrane casting solution. By treating the fiber casting polymer solution as a colloidal system, data on its viscosity may be expected to offer insight into the solution structure of the system, reflecting the size and disposition of the polymer molecules in the system. Therefore, the viscosity of all the fiber casting solutions used were determined prior to membrane making. Data on viscosities are included in Table 2. With respect to the experimental data on viscosity, two significant observations were made. The viscosity of the fiber casting polymer solution increased upon storage for a few weeks, and decreased after filtration prior to use in fiber making. In Table 2, Fibers 11, 12, and 13 were made with unfiltered fiber casting polymer solutions; the viscosity data are for such unfiltered solutions. All other fibers listed in Table 2 were made with filtered fiber casting solutions, and their viscosity data are for filtered solutions.

Figures 7 and 8 compare the performance data [i.e., PEG separation (f) vs PEG molecular weight, and (average) PR] for a number of fibers produced in this work under different experimental conditions specified in Table 2, which also includes data on their physical dimensions, NFV, V_P, and V_W values. In all the experiments reported herein, the extrusion pressure used was 5 psig.

Figure 7(a) gives f and PR values for the Fibers 1, 5, and 13 (obtained with M1 solution composition) for which WFR and LAG values were 10 mL/min and 80 cm, respectively. Fibers 1 and 5 were produced using filtered polymer solutions stored for 0 and 1 week, respectively, prior to filtration. Fiber 13 was produced with unfiltered polymer solution stored for 5 weeks prior to use in fiber production. All other conditions of fiber production remained the same. It should be noted that the viscosities of the solutions used for the production of Fibers 1, 5, and 13 were 2314, 2710, and 2815 mPa·s (cP), respectively. The performance data show that f values for Fibers 5 and 13 were nearly identical and significantly higher than those of Fiber 1, while the corresponding PR value for Fiber 1 was higher than that of both Fibers 5 and 13. The results indicate that the average size of pores on the skin layer of Fibers 5 and 13 was significantly smaller than that of Fiber 1, and the effective number of pores on the skin layer (equivalent to a thinner skin layer and/or larger number of skin layer pores) of Fiber 13 was even higher than that of Fiber 5, which is obviously a combined effect of longer duration of solution storage and fiber casting solution used without prefiltration, thus the consequent increase in solution viscosity. It may be noted that Fibers 5 and 13 had a molecular weight cut-off (MWCO) for PEG-2500, whereas Fiber 1 may have one for PEG-10,000.

The corresponding data on fiber physical dimensions in Table 2 for Fibers 1 and 5 show that increasing the storage time from 0 to 1 week yielded fibers with higher o.d., i.d., wall thickness, and o.d./i.d. ratio.

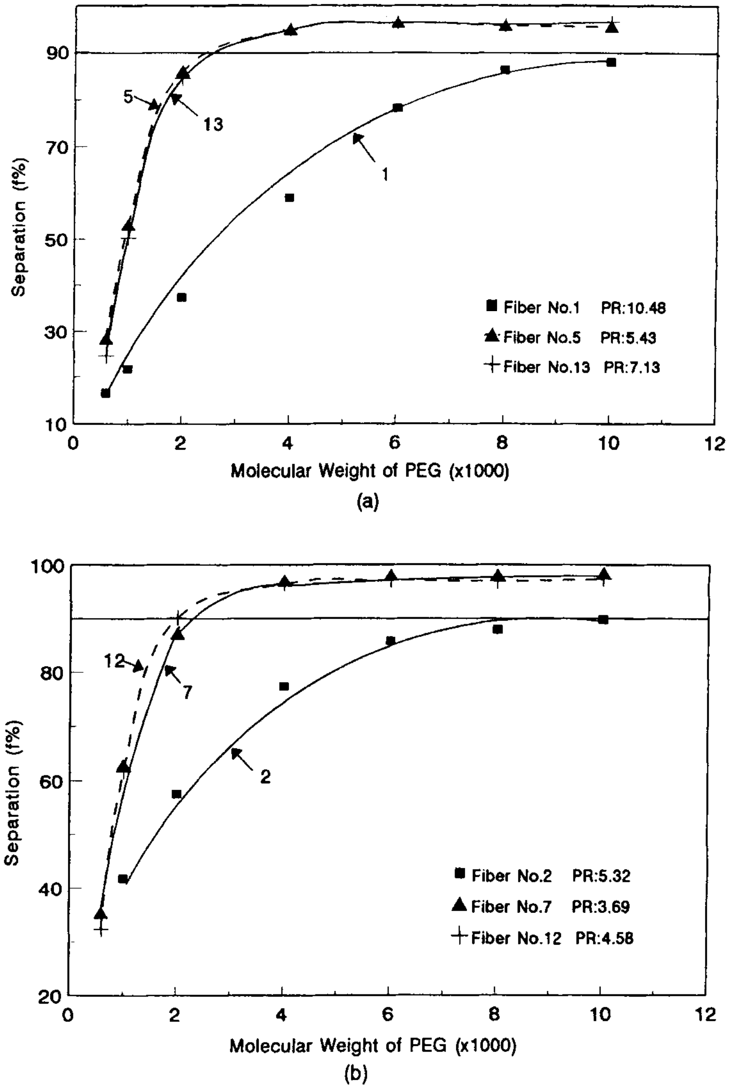


FIG. 7 Effect of storage time of the casting solution on solute separation.

Figure 7(b) gives *f* and PR data for Fibers 2, 7, and 12 which differ from Fibers 1, 5 and 13 (Figure 7a) with respect to storage period, and/or WFR used. [The difference in the viscosity (Table 2) for Fibers 5 and 7 appears to be due to the possible difference in the weave of the filter cloth used.] Figures 7(a) and 7(b) show similar performance results. The separation (f) values for Fibers 7 and 12 were nearly identical and significantly higher than those of Fiber 2. The PR value for Fiber 2 was relatively higher than that of both Fibers 7 and 12; and again the productivity of Fiber 12 (which was produced using an unfiltered fiber casting solution) was significantly higher than that of Fiber 7. The MWCO values for Fibers 7 and 12 were PEG-2200 and PEG-2000, respectively, a little smaller than the MWCO value obtained for Fibers 5 and 13. These data indicate that the average pore sizes on the skin layer of Fibers 7 and 12 were even smaller than those of Fibers 5 and 13.

Data on fiber physical dimensions for Fibers 2 and 7 (Table 2) also show that increasing storage time tends to yield fibers with higher o.d., wall thickness, and o.d./i.d. ratio.

Figures 8 shows explicitly the effect of not prefiltering the fiber casting polymer solution on the performance of the resulting membranes. Fibers 8, 9, and 10 were produced with filtered solutions, and Fibers 11, 12 and 13 were produced with unfiltered solutions. In all cases the unfiltered solutions yielded fibers with smaller average size pores on the skin layer of the membranes, and hence higher PEG separations under otherwise comparable experimental conditions of fiber production. The data of MWCO and PR values are particularly interesting.

Figure 8(a) compares the performances of Fibers 10 and 11 produced with filtered and unfiltered solutions, respectively; all the other experimental conditions of fiber production remained the same. The results show that the PR value for Fiber 11 was only slightly less than that for Fiber 10, even though the PEG separation obtained with Fiber 11 was significantly higher. These results indicate that without prefiltration the fiber casting solution resulted not only in smaller size pores on the skin layer of the membrane but also a larger number of such pores and/or a lesser skin layer thickness. The MWCO values for Fibers 10 and 11 were PEG-10,000 and PEG-2200, respectively.

The foregoing conclusion regarding the size and effective number of skin layer pores is supported by the results presented in Fig. 8(b) for Fibers 9 and 12 obtained at a different LAG (80 cm). These results show that Fiber 12, produced from unfiltered solution, gave not only higher f values for PEG solutes but also a higher PR value. Therefore, combined with appropriate choices of other fiber production conditions, an unfiltered fiber casting polymer solution can yield fibers with both higher f and higher PR simultaneously. The MWCO values for Fibers 9 and 12 were PEG-3000 and PEG-2000, respectively, significantly lower than those obtained (Fig. 8a) at a lower LAG (50 cm).

Figure 8(c) present data on the performance of Fibers 8 and 13 produced from filtered and unfiltered solutions, respectively. These data are similar to those presented earlier (Figs. 8a and 8b). In addition, Fig. 8(c) illustrates the effect of an increase in WFR on fiber performance. The MWCO for Fibers 8 and 13 are PEG-4800 and PEG-2600, respectively, which indicate that the pore sizes on the skin layer of Fibers 8 and 13 were bigger than those of Fibers 9 and 12, respectively. The observed increase in PR for Fibers 8 and 13 (compared to those for Fibers 9 and 12) is consistent with the above conclusion.

A review on fiber physical dimensions of Fibers 10 and 11, 9 and 12, and 8 and 13 (Table 2) leads to no definite conclusion on the effect of prefiltration or no prefiltration of the fiber casting polymer solution on o.d., i.d., wall thickness, and o.d./i.d. values of the resulting fibers. Variations in these quantities seem to depend on a combined effect of solution composition, viscosity, WFR, LAG, etc. rather than uniquely by prefiltration or no prefiltration of the fiber casting polymer solution.

The experimental data presented in Figs. 7 and 8 clearly show that storage time, with prefiltration or no prefiltration of the fiber casting polymer solution, and the consequent change in solution viscosity have significant effects on the performance characteristics of the resulting membranes. Therefore, from the point of view of standardization of HF production, the foregoing preparation conditions should be specified in as much detail as possible.

Effect of Polymer (PES) Concentration on Membrane Performance

An increase in solution viscosity can also be induced by increasing the polymer concentration in the fiber casting solution. Therefore a set of experiments was carried out to see how membrane performance was affected by viscosity increase. The results are shown in Fig. 9 and Table 2 with Fibers 2, 14, and 17 made from solutions M1, M2, and M3, respectively. It is important to note that all three fibers were produced from filtered solutions with zero storage time.

The PES concentrations in M1, M2, and M3 were 20, 22, and 24 wt%, respectively, and their corresponding viscosities were 2314, 3590, and 7744 mPa·s. The relative magnitude of the viscosity increases as a result of an increase in polymer concentration was far higher compared to unfiltered M1 or an increase in its storage time. Performance results from fibers produced from the higher viscosity M2 and M3 solutions, when compared with those obtained with filtered M1 solution, should offer some indication regarding the structure of unfiltered and/or stored M1 fiber casting solutions.

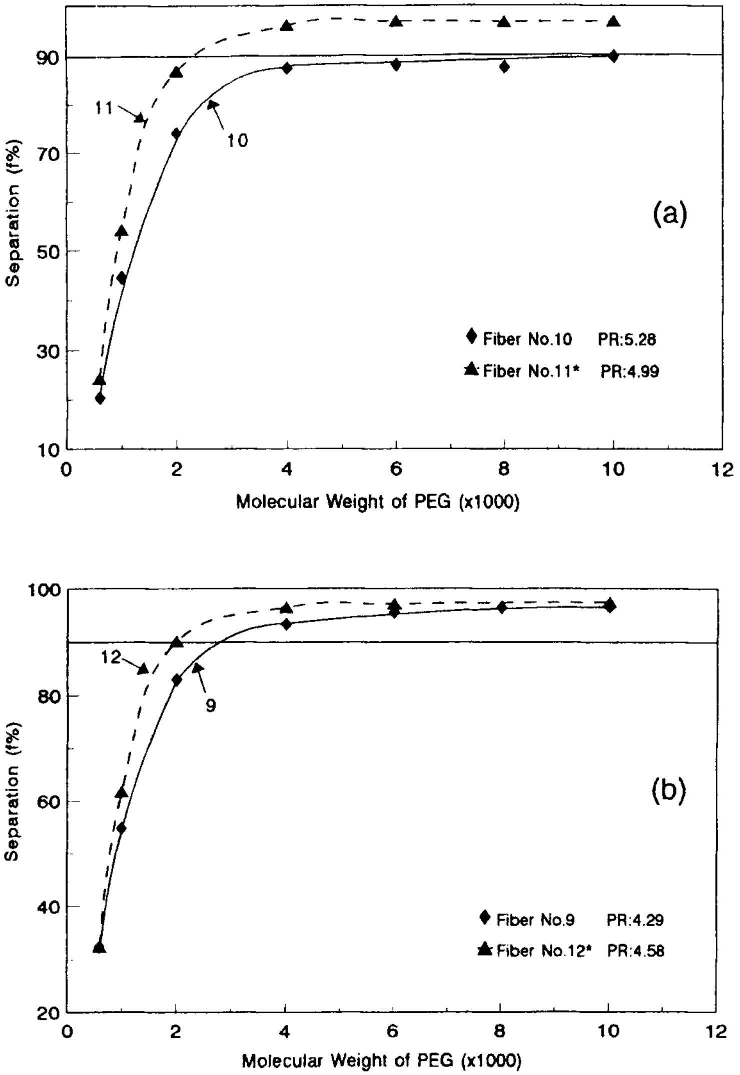
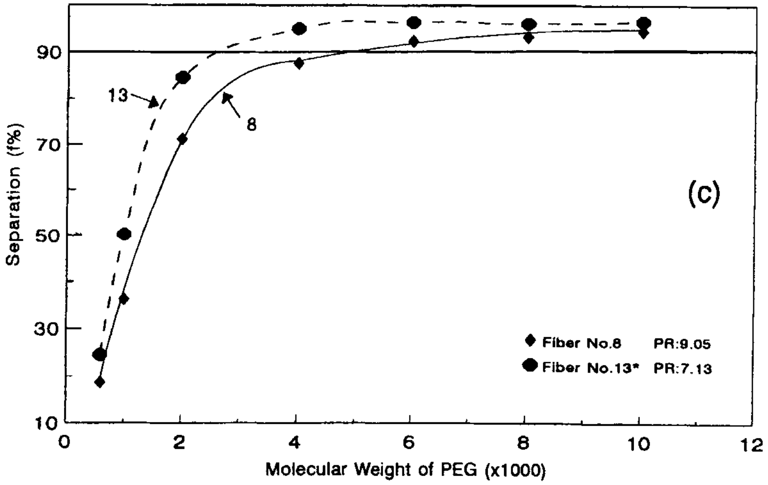


FIG. 8 Effect of casting solution with prefiltration/without prefiltration on solute separation.

Figure 9 shows that both PEG separations and PR values are relatively higher for Fibers 14 and 17 compared to those for Fiber 2, which indicate that performance of membranes made from the higher viscosity M2 and M3 solutions is similar to those of membranes made from unfiltered and/or stored M1 solution shown in Figs. 7 and 8. These results indicate that



(*:Fibers 11, 12 and 13 from unfiltered solutions.)

FIG. 8 Continued

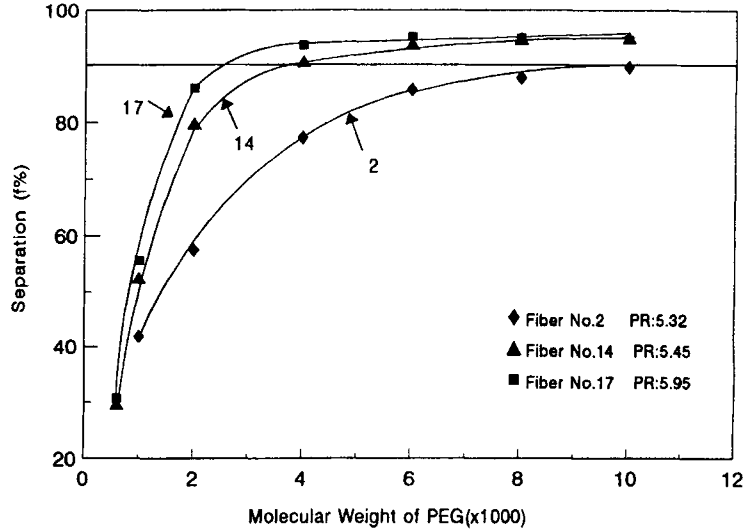


FIG. 9 Effect of PES concentration in casting solution on solute separation.

changes in polymer solution structure in both cases, as manifested by viscosity increases, are also similar, at least in part, as it is known that higher polymer concentration in the casting solution yields membranes with smaller size pores on the surface of the resulting membranes (11).

Viscosity and Polymer Solution Structure

The fiber casting polymer solution is a heterogeneous colloidal system in which domains of high and low density exist. The apparent viscosity of such a colloidal system offers insight into the structure of the polymer solution (i.e., the size and disposition of the polymer particles in the fiber casting solution). The suspended polymer particles tend to link up to form a more extended network of large, loose, ramifying aggregates in the entire solution region during storage for extended periods (12). Such ramifying structural aggregation immobilizes much of the solvent and imparts greater rigidity to the colloidal suspension as a whole, which accounts for its increased viscosity. The apparent viscosity of the fiber casting solution is thus a structural viscosity. The consequence of such ramifying, structural aggregation is the formation of network pores in the incipient state in the fiber casting solution. This accounts for the decrease in average pore size in the skin layer of the membranes made from fiber casting solutions stored for extended periods, as illustrated in Figs. 7(a) and 7(b). The above sequence of events is also expected to occur in unfiltered fiber casting solutions, as suggested by evidence in Figs. 7 and 8.

On the other hand, during filtration of a fiber casting polymer solution, the extended structural network of polymer particles created during solution formation is partly disrupted (or otherwise removed), as manifested by a decrease in viscosity of the filtered solution. Such disruption of the polymer solution structure gives rise to a larger number of discrete polymer aggregates, and hence incipient aggregate pores, in the fiber casing solution. Using such a solution for fiber casting, these aggregates yield bigger aggregate pores on the skin layer of the resulting membrane (7) as shown explicitly by the data given in Fig. 8.

The foregoing discussion points out that the structure of the fiber casting polymer solution is an important parameter governing fiber morphology; further, polymer solution structure is not only a function of composition of the solution and its temperature, but also depends on the precise state of ramifying structural aggregation in the polymer solution. The latter is affected by several variables involved in solution preparation such as storage time and filtration details, and possibly others. Hence these variables need to be specified in as much detail as possible in order to standardize the conditions of fiber production.

CONCLUSION

Standardization in the production of PES hollow fiber UF membranes would involve at least two major requirements.

First, the fiber testing conditions should be fully comparable. This requires that the length of each test fiber, the average UF operating pressure used, the pressure drop in the fiber bundle, and the feed flow velocity in the fiber bore are held constant during the test. Further, the obtainable mass transfer coefficient (which is also governed by surface roughness) as a function of feed flow velocity through the fiber bore should be determined and recorded for a reference solute, such as PEG-1000, in very dilute aqueous solution.

The second requirement is concerned with the structure of the fiber casting polymer solution which is an important parameter governing the ultimate fiber morphology. The solution structure is governed by several variables involved in solution preparation. These variables include, besides the overall composition and temperature of the solution, the time for which the solution was held in storage and whether or not the solution was filtered prior to fiber casting. In addition, the above variables may also include details such as the mixing technique used in solution preparation. Therefore, the method of preparation of the fiber casting solution needs to be specified in as much detail as possible for the production of reproducible and unique PES HF UF membranes.

Though the foregoing standardization requirements have been illustrated in this work with particular reference to PES HF membranes, they are also generally applicable to the production and testing of all HF UF membranes.

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