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Characterization of morphology controlled polyethersulfone hollow fiber membranes by the addition of polyethylene glycol to the dope and bore liquid solution

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Abstract

The preparation of polyethersulfone (PES) hollow fiber membranes has been studied using *N*-methylpyrrolidone (NMP) as solvent, polyethylene glycol 400 (PEG 400) as weak nonsolvent and water as strong nonsolvent. When PEG 400 is used as polymeric additive to the spinning dope the viscosity of the PES solution is strongly enhanced. Furthermore, it was observed that PEG 400 could be added to the solution in large amounts without causing phase separation (NMP/PEG ratio 1:9, PES concentration approximately 11 wt.%). Membranes prepared from a solution containing a NMP/PEG ratio of 1:1 results in higher fluxes than when a ratio of 1:4 is used. Similar fluxes were obtained for PES concentrations of 16 and 20 wt.%. Looking at the fiber cross-section it became clear that macrovoid formation could not be suppressed by the addition of PEG 400 alone, not even at concentrations as high as 38 wt.%. Only when relatively large amounts of water were added to the dope solution macrovoids disappeared and nice spongy structures were obtained. Variation of the bore liquid composition using the components NMP, PEG 400 and water showed to be a powerful method to control the pore size of the bore surface. Pores of 5–28 nm were obtained in combination with high pure water fluxes; e.g. a membrane with pores of 7 nm had a pure water flux of 940 l/(m² h bar) and showed 100% BSA retention. When an air gap larger than 10 mm was applied the shell surface contained relatively large pores. Spinning directly in water (air gap = 0) resulted in shell side pores of 8–10 nm, while an air gap of 10 mm resulted in pore sizes of 40–54 nm.

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1. Introduction

Polysulfone (PSF) and polyethersulfone (PES) have been used by many researchers [1–7] in the preparation of hollow fiber membranes as membrane forming

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material. The membrane forming process followed in the preparation of PSF and PES hollow fibers is always the phase separation process, where a homogeneous polymer solution precipitates in a nonsolvent bath. In phase separation processes thermodynamic and kinetic processes play an important role in structure formation. Thermodynamics determine whether a polymer solution is homogeneous and stable or inhomogeneous and likes to phase separate. The starting situation is

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normally a homogeneous solution, which is forced to phase separate by changing its composition when immersed in a nonsolvent bath. Kinetic processes play a key role in this transition. The ratio in-diffusion of nonsolvent and out-diffusion of solvent govern the ultimate membrane structure to a large extent. The driving forces for the diffusion of solvent and nonsolvent are determined by the solvent and nonsolvent concentrations in the polymer solution and the coagulation bath. By playing with the solvent/nonsolvent ratio in both the polymer solution and the coagulation bath the kinetics of phase separation can be manipulated and hence the membrane structure [8].

The most frequently used solvents are *N*-methylpyrrolidone (NMP), dimethyl acetamide (DMAc), dimethylformamide (DMF), dimethylsulfoxide (DMSO), γ -butyrolactone and ε -caprolactam. The coagulation bath is often water or a mixture of water and solvent.

Another frequently applied method to influence the membrane structure is the use of additives in the polymer solution. The role of these additives a.o., is to create a spongy membrane structure by prevention of macrovoid formation, enhance pore formation, improve pore interconnectivity and/or introduce hydrophylicity. Hydrophilic structures are obtained by the addition of, e.g. polyvinylpyrrolidone (PVP). Other frequently used additives are: glycerol, alcohols, dialcohols, water, polyethylene glycols (PEG), polyethylene oxide (PEO), LiCl and ZnCl₂.

Most hollow fiber membranes are prepared by the so-called dry-wet spinning process and only few have been prepared by a wet-wet or dual bath spinning process [4-6]. The wet-wet spinning process can be very well applied for controlling the shell side surface structure. In this process the nascent fiber is brought into brief contact with a first coagulant, after which the fiber enters the coagulation bath (second coagulant). The choice of the first coagulant determines the ultimate structure. When a weak nonsolvent is applied, like e.g. glycerol completely dense skin layers can be obtained supported by a porous sub-structure, which make the membrane suitable for gas separation [4,6]and pervaporation [5]. Here, the diffusion of solvent out of the nascent fiber is much higher than the diffusion of nonsolvent into the nascent fiber.

When a mixture of solvent and strong nonsolvent, e.g. *N*-methylpyrrolidone and water, is applied extremely open surface layers can be obtained [7,8]. The solvent/nonsolvent composition is a powerful parameter to influence the pore size of a membrane. The diffusion of solvent out of the nascent fiber is retarded by the presence of solvent in the coagulation bath. When the solvent concentration in the coagulation bath is higher than in the nascent fiber solvent might even diffuse into the nascent fiber, diluting the polymer concentration prior to phase separation. Proper application of the wet–wet spinning process requires a triple-layer spinneret; the bore liquid composition controls the inside structure, while the outside liquid composition controls the structure of the shell side [5–7].

A tube-in-orifice spinneret is normally applied in the dry–wet spinning process. Here, the nascent fiber first travels an air gap before it enters the coagulation bath. The shell surface structure can now be controlled by the air gap length and environment of the air gap (humidity, temperature, presence of organic vapor). The inside surface structure is mainly controlled by the bore liquid composition as in the wet–wet spinning process.

Preferably one would like to have a spongy membrane structure without macovoids. This normally results in mechanically more stable membranes. Macrovoid formation in phase separation occurs from freshly formed nuclei of the diluted phase when the composition in front of the nuclei remains stable for a relatively long period of time [9,10]. Due to diffusion of solvent expelled from the surrounding polymer solution the macrovoid grows. Macrovoids are generally formed in systems where instantaneous demixing takes place, except when the polymer additive (e.g. PVP) concentration and/or the nonsolvent concentration in the polymer solution exceed a certain minimum value [9-12]. Therefore, a dope composition close to the binodal composition favors the formation of spongy structures.

In this study, hollow fiber membranes were developed using polyethersulfone as membrane material, NMP as solvent and PEG 400 as polymeric additive. PEG as additive is less frequently used [13–16] compared to PVP, but could play a similar role in the formation process; i.e. as macrovoid suppressor and giving the membrane a hydrophilic character. Xu et al. [14] showed by a reduction of the T_g of a PEI/PEG membrane that PEG 600 remains inside the polyetherimide matrix and therefore gives the membrane a hydrophilic character. The PEG concentration used by Xu et al. [14] was only 5 wt.%, while in this study PEG concentrations between 37 and 64 wt.% are used. They also observed the more open the structure the less PEG remains inside the ultimate membrane. A secondary role of the PEG could be the role of pore former and macrovoid suppressor.

Here, the effect of PEG 400 as well as the addition of water to the polymer spinning dope on the suppression of macrovoid formation is studied. Furthermore, this paper shows how the pore size of the inside membrane surface and the outside membrane surface can be controlled independently and that high flux membranes with ultrafiltration characteristics (pore size 2–50 nm) can be prepared. Applications for these fibers can be found in the preparation of composite membranes, where the fibers serve as porous support or in ordinary ultrafiltration.

2. Materials

Polyethersulfone (PES) was purchased from BASF (Ultrason E6010P), *N*-methyl-2-pyrrolidone (NMP) synthetic grade was purchased from Merck and used without further purification as solvent. Polyethylene glycol (PEG 400) for synthesis was supplied by Merck and used as additive. The water used in the bore liquid during spinning and in pure water flux experiments was deionized by a Milli-Q system (18 M Ω cm). BSA ($M_w = 67,000$ g/mol) was purchased from Sigma.

3. Experimental

3.1. Cloud point measurements

Cloud point data to determine the binodal composition of the PES/PEG 400/NMP/water system were measured by means of a titration method. Pure water was slowly added to a solution of polymer and solvent. The solution was kept at a constant temperature. Every drop of water added to the solution caused local coagulation. Further addition of water was performed after the solution became homogeneous again. This procedure was continued until permanent turbidity was detected visually. In the preparation of polymeric membranes normally a homogeneous polymer solution is used. Therefore, smaller amounts of water necessary to cause phase separation are added to the dope solution used in membrane preparation. The ratio of water added and the amount required to reach phase separation is defined as the coagulation value.

3.2. The spinning process

The spinning set-up used in our work is the same as used by Wienk et al. [7]. PES and PEG were dissolved in NMP and water was added. The polymer solutions were filtered by a metal filter $(25 \,\mu\text{m})$ and were degassed prior to fiber spinning. After coagulation the fibers were rinsed with water for 2 days followed by immersion in an aqueous 10 wt.% glycerol solution for another 24 h. Then the fibers were dried in air.

The temperature of the polymer solution, coagulation bath and bore liquid were kept constant at 20 ± 2 °C. The extrusion rate of the polymer solution and take-up speed of the fibers was kept constant as well. The take-up speed was generally around 5 m/min. In this study only the air gap length and bore liquid composition were varied in order to control the pore size of the fiber inside and outside surface. However, the authors do not claim that these are the only parameters that affect the pore size.

3.3. Viscosity measurement

The viscosity of the spinning solutions was determined using a viscosity meter (Brabender Viscotron Rotation Viscosity Meter) at constant temperature. Measurements were performed at different shear rates and the values reported correspond to values obtained by extrapolation to zero shear rate and at 25 $^{\circ}$ C.

3.4. Pure water flux measurement

Pure water flux experiments were performed using deionized water prepared by a Milli-Q system (18 M Ω cm). Small modules consisting of several fibers of a length of 30 cm were constructed with a total surface area of approximately 20 cm². The transmembrane pressure applied was 0.9 bar and the experiments were performed in a dead-end mode.

3.5. BSA retention measurement

BSA retention was measured using 0.1 wt.% BSA in a phosphate buffer solution of pH 7.4, containing 0.1 M NaCl. The filtration experiments were carried out in a normal cross-flow filtration set-up. For membranes with the separating layer at the shell side the feed was fed outside in. When the separating layer was at the bore side of the fiber the feed was fed inside-out. The tested modules consisted of eight fibers with a total membrane area of about 35 cm^2 . The applied transmembrane pressure was 1.0 bar. After 30 min of permeation the water flux was practically constant. BSA concentrations were determined by a spectrophotometer (PU8700 Series, UV-Vis Spectrophotometer, PHILIPS) at 280 nm. The retention *R* was calculated according to the formula:

$$R = \left(1 - \frac{C_{\rm p}}{C_{\rm f}}\right) \times 100\% \tag{1}$$

where C_p and C_f represent the BSA concentration in the permeate and in the feed, respectively.

3.6. SEM analysis

Scanning electron microscopy (Jeol, JSM T220A) was applied to study the morphology of the hollow fiber membranes. To study the cross-section of the fibers samples were prepared by cryogenic fracturing. At first, the fibers were immersed in ethanol for about 10 min, after which the fibers were frozen in liquid nitrogen and broken. To study the inner and outer surface the fibers were carefully cut in halve in the direction of length and fixed on a sample holder using conductive glue. After drying under vacuum the samples were coated with a thin gold layer using a sputter apparatus (Balzers Union SCD 040). Now the samples are ready for use.

3.7. Pore size determination by permporometry

Permporometry appears to be an excellent technique to measure the pore size and pore size distribution of dry meso-porous membranes (2–50 nm). After the introduction of permporometry by Katz et al. in 1982 [17,18] only few publications followed [19–21]. However, no results have been reported on hollow fiber materials so far.

One of these publications is by Cuperus et al. [21]. He describes a method based on controlled blocking of the pores by condensation of organic vapor (e.g. cyclohexane or ethanol) and simultaneously measuring a gas flux through the open pores. The driving force for gas transport is created by a partial pressure difference across the membrane, while maintaining atmospheric pressure at both sides of the membrane. The Kelvin relation describes the relationship between the vapor activity or relative vapor pressure and the pore radius. The gas flux through the membrane is a measure for the number of open pores. The Kelvin relation is expressed by

$$\ln\left(\frac{p_{\rm v}}{p_{\rm v}^{\rm o}}\right) = -\frac{\gamma V_{\rm m}}{RT}\cos\phi\left(\frac{1}{r_{\rm K_1}} + \frac{1}{r_{\rm K_2}}\right) \tag{2}$$

Here, p_v represents the actual gas pressure (Pa), p_v^o the saturation pressure (Pa), γ the interfacial tension (N m⁻¹) of the condensed gas, V_m the molar volume (m³ mol⁻¹), R the ideal gas constant (J mol⁻¹ K⁻¹), T the temperature (K), ϕ the contact angle between the condensed vapor and the polymer (°) and r_{K_1} and r_{K_2} are the Kelvin radii (m) of the curvature of the gas–liquid interface inside the pore. In the desorption mode r_{K_1} equals r_{K_2} and when the condensed vapor wets the pore wall completely $\cos \phi$ equals 1.

The technique applied in this paper resembles the method proposed by Cuperus et al. [21] the best. The vapor activity in the feed stream and permeate stream were controlled by mass flow controllers. Both streams are composed of two other streams, one completely saturated with the organic vapor and one absolutely vapor free. When the two streams are brought together the ratio of the streams determines the vapor activity. As carrier gas in the feed stream air was used while pure nitrogen was used as carrier gas at the permeate side, see also Fig. 1. It is important to have identical vapor activities at the feed and permeate side. The organic vapor used was cyclohexane (has negligible interaction with the membrane material polyethersulfone) and the transmembrane pressure during the



Fig. 1. Schematic representation of the permporometry set-up.

measurement was equal to zero, only a partial pressure difference of oxygen and nitrogen was present. The set-up used is schematically represented in Fig. 1.

A drawback of this technique is that dry membranes have to be used. Normally, when UF membranes are dried from an aqueous solution the structure of the separation layer may collapse. Capillary forces on small pores when water evaporates can be enormous and is described by the La Place relation.

$$r_{\rm p} = \frac{2\gamma\cos\theta}{P} \tag{3}$$

Reducing the interfacial tension, γ , will reduce the pressure, P, on the pore wall. By solvent exchange pore collapse due to capillary forces can be controlled to some extent. Therefore, a solvent exchange procedure was applied in this study to measure a representative as possible pore size.

3.8. Research strategy

To reach the target of this paper, viz. UF hollow fiber membranes with spongy structures and controlled pore size on shell and bore side using a PES/PEG blend, the following procedure was followed:

- At first a dope composition was selected that results in spongy structures. Therefore, the binodal composition of four different PES/PEG/NMP/water solutions were determined.
- Based on the binodal composition five different PES/PEG/NMP/water spinning solutions were prepared. These solutions differ from the binodal composition in their water content. The water content is a little bit lower in order to obtain homogeneous polymer solutions.
- Five batches of hollow fibers were spun using the five different spinning dopes. In all experiments the air gap was 10 mm and the bore liquid was pure water. Based on the structure and the pure water flux of these fibers the most promising dope composition was selected for further research.
- Now the influence of the pore size of the bore side was studied by varying the bore liquid composition. Mixtures of water/NMP/PEG were applied.
- Finally, the effect of the air gap length on the pore size of the shell side is studied.

4. Results and discussion

It is very common to add components like polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), tetra ethylene glycol (TEG), LiCl, etc. to polymer solutions used in membrane preparation. These components often have various tasks, as to: increase the viscosity, introduce hydrophilicity, improve pore formation and suppress macrovoid formation. Besides these additives water is often added as well to bring the solution composition closer to the binodal composition.

Here, PEG 400 was used as additive to improve the pore formation and pore interconnectivity in order to create membranes with high pure water fluxes. PEG is a very weak nonsolvent and can be added in large amounts to PES/NMP solutions. Starting with a 20 wt.% PES in NMP solution PEG could be added up to a ratio of 9:1 PEG:NMP. The PES concentration reduced to 11.1 wt.% and the solution was still perfectly homogeneous and clear.

4.1. Binodal composition and spinning solutions

Several homogeneous polyethersulfone solutions have been prepared based on PEG, NMP and water. Two PES concentrations, 16 and 20 wt.%, and two NMP:PEG ratios, 1:1 and 1:4 were chosen.

At first the binodal composition of the four possible combinations was determined by the controlled addition of water. Then several spinning solutions have been formulated with compositions in the homogeneous and stable region of the phase diagram, not too far away from the binodal composition. Table 1 shows the binodal composition of several PES solutions and Table 2 lists the spinning dope composition and viscosity of the solutions used for membrane preparation in this study.

Table 1 Binodal composition of several PES solutions

Solution	PES	NMP	PEG	Water
	(wt.%)	(wt.%)	(wt.%)	(wt.%)
Binodal I	16	38.35	38.35	7.3
Binodal II	20	36.65	36.65	6.7
Binodal III	16	15.88	63.52	4.6
Binodal IV	20	15.36	61.44	3.2

spinning dope composition of various solutions							
Solution	PES (wt.%)	NMP (wt.%)	PEG (wt.%)	Water (wt.%)	Coagulation value (%)	Viscosity 25 °C, (C_p)	
A	20	37.70	37.70	4.60	68.7	28000	
В	20	36.90	36.90	6.20	92.5	37500	
С	20	15.44	61.76	2.80	87.5	72100	
D	16	16.00	63.84	4.20	91.3	23800	
E	16	38.50	38.50	7.00	95.9	9350	

Table 2 Spinning dope composition of various solutions

A polymer solution with a nonsolvent content lower than the amount needed to cause phase separation can be characterized by a coagulation value, which is always smaller than one. When, e.g. a polymer solution of 20 wt.% PES in NMP/PEG (1:1) requires 6.7 wt.% water to cause phase separation (see Table 1, binodal II), than a polymer solution of 20 wt.% PES in NMP/PEG (1:1) with 6.2 wt.% water has a coagulation value of 92.5%.

From the data in Table 2 it can be clearly seen that the addition of PEG 400 increases the viscosity of the dope.

4.2. Selection of the best spinning solution

Next, five different hollow fiber membranes have been spun using the five different PES solutions as presented in Table 2. Three solutions contained 20 wt.% PES and two contained 16 wt.% PES. Solutions B–E have a composition close to the binodal composition (coagulation values between 87.5 and 95.9%), while the composition of solution A lies much further away from the binodal and has a coagulation value of 68.7%. The air gap in the spinning process was 10 mm and pure water was used as bore liquid. Table 3 shows the pure water fluxes of the five different membranes as

Table 3

Pure water flux and membrane structure as a function of PEG content and PES content in the dope solution

ux Membrane structure
Macrovoids
Spongy
Spongy
Spongy
Spongy

well as the presence of macrovoids. A macrovoid free structure combined with high flux is desirable.

4.2.1. Influence of coagulation value on the formation of macrovoids

Two of the spinning dope solutions listed in Table 2 (A and B) are rather similar in composition, but differ in coagulation value. Solution A has a coagulation value of 68.7% and solution B has a coagulation value of 92.5%. Both solutions have a PEG/NMP ratio of 1:1 and a PES concentration of 20 wt.%. Hollow fiber membranes were prepared applying various NMP/water mixtures as bore liquid. Under all conditions the hollow fibers prepared from dope A, with the lower coagulation value, always resulted in membrane structures with macrovoids. Dope B, with a coagulation value above 90% always resulted in spongy structures (see Fig. 2). According to Smolders and coworkers [10] macrovoid formation takes place in systems showing instantaneous demixing. Based on that statement one expects macrovoids in the structure formed from both dope solutions. However, the authors also state three exceptions, viz. (i) macrovoid formation can be suppressed when the polymer concentration exceeds a certain minimum value, (ii) macrovoid formation can be suppressed when the nonsolvent concentration in the polymer solution exceeds a certain minimum value and (iii) macrovoid formation can be suppressed by the presence of a second polymer in the polymer solution. In the latter situation the molecular weight of the second polymer should be sufficiently high and the concentration should again exceed a certain minimum value. The molecular weight of the PEG 400 is not sufficiently high to suppress macrovoid formation by itself. Macrovoids were still present when relatively low amounts of water were added, even though the PEG content was 37.7 wt.% (solution A). Since the polyethersulfone concentration



Fig. 2. Cross-section of hollow fiber spun with dope A, coagulation value 68.7% (A) and dope B, coagulation value 92.5% (B); it shows the influence of the coagulation value on the presence of macrovoids.

and the PEG concentration are equal in both solutions the suppression of macrovoids using dope B should be attributed to the presence of a relatively high content of nonsolvent (water) in dope B. Furthermore, it can be seen from Table 3 that all dope solutions with a coagulation value >87.5% result in spongy structures. Therefore, it is advised to use a dope solution with a coagulation value >90% to be sure that spongy and macrovoid free structures are obtained.

4.2.2. Influence of PES concentration and NMP/PEG ratio

From Table 3, it can also be concluded that the PES concentration does not have so much influence on the pure water flux. The concentration of PEG on the contrary has a large influence. Kim and Lee [13] showed that the pure water flux increases exponentially with increasing PEG/NMP ratio up to a ratio of 1:1. Here, the PEG/NMP ratio was increased even higher, but results in a lower pure water flux at a ratio of 4:1 compared to a ratio of 1:1. The optimum ratio PEG/NMP seems to be around 1:1. For further membrane optimization the spinning solution E with 16 wt.% PES and a NMP/PEG ratio of 1:1 was selected as the most promising. To check the presence of PEG 400 in the hollow fiber membrane after formation the $T_{\rm g}$ was determined of the fibers prepared with dope E. The $T_{\rm g}$ of these fibers ($T_g = 184 \,^{\circ}$ C) was significantly reduced compared to the T_g of pure PES ($T_g = 230 \,^{\circ}\text{C}$) and only one T_g was observed. This implies that PEG 400 is still present in the ultimate fiber and forms a homogeneous blend with PES.

4.3. Pore size determination

Before the study on pore size control started a method to measure the pore size in meso-porous hollow fiber membranes was developed. The permporometry technique was applied, and a set-up had to be constructed, verified and adapted for hollow fibers. Until now this method was only applied for flat sheet membranes.

A schematic representation of the set-up can be seen in Fig. 1. To validate the set-up and method applied the pore size distribution curves of two different flat sheet track-etch membranes (pore diameter 15 nm and pore diameter 50 nm) were analyzed. The obtained pore size distribution curves are presented in Fig. 3. It can be concluded that the obtained average pore size corresponds very well with the pore diameter given by the manufacturer.

To be able to characterize the hollow fiber membranes small modules, containing five fibers of a length of approximately 5 cm were prepared. To remove the glycerol from the pores the modules were rinsed with pure water. Then the water was replaced by ethanol, followed by flushing with hexane. Finally, the modules were carefully dried in air and placed in the Permporometry set-up for pore size analysis. This, however, does not guarantee that the porous structure



Fig. 3. Pore size distribution curves of two different track-etched membranes. (A) Nuclepore membrane with pore diameter of 15 nm; (B) Whatman membrane with pore diameter of 50 nm. The dots represent fitted data.

is not altered at all by this procedure. Nevertheless, a relative comparison seems fair enough since all fibers were treated in the same way and a clear influence of membrane preparation conditions on the ultimate mean pore size measured by permporometry could be obtained, as will be shown in the following paragraphs.

4.3.1. The measurement protocol

At first the pores were blocked applying a cyclohexane activity of 0.95. Then step-wise the activity was lowered and the oxygen flux through the membrane was measured by analyzing the permeate and feed stream using a GC. After each vapor activity change the system was given 1 h to reach steady-state conditions, followed by three feed and three permeate analysis. For each pore size distribution curve the oxygen permeation was measured at 10–15 different activities. The whole measurement was automized (Labview) and took place in an air-conditioned room (20 °C). An example of a curve describing the accumulated oxygen flux as a function of the vapor activity or better pore radius is given in Fig. 4A. Fig. 4B shows the derivative of the curve in Fig. 4A as a function of the pore radius, and represents the pore size distribution curve. The dots represent the measured values and the line is a mathematical fitting of the data points. The plots in



Fig. 4. Accumulated oxygen flux as a function of the pore radius (A) and its derivative as a function of the pore radius (B); dots correspond to measured data, line corresponds to data fit (example of a hollow fiber analysis; corresponds to the 2nd fiber presented in Table 4).

Table 4

The effect of the bore liquid composition on the pure water flux, BSA retention and pore size of various hollow fiber membranes prepared from spinning dope E

Lumen composition		Air gap	Pure water flux	BSA retention	Pore diameter	SEM photo no.	
Water (wt.%)	NMP (wt.%)	PEG (wt.%)	(mm)	(l/(m ² h bar))	(%)	(nm)	(Fig. 5)
100	0	0	10	412	100	5	A
70	0	30	10	940	100	7	В
40	30	30	10	1400	91	15	С
26	37	37	160	1115	55	28	D

Fig. 4 represent the pore size distribution of the second fiber presented in Table 4 (pore diameter = 7 nm).

4.4. Hollow fiber membranes with controlled pore size of the inside surface

Now hollow fiber membranes with inside skin were produced using solution E as spinning solution. The inside skin structure was controlled by variation of the bore liquid composition. The components used in the bore liquid were water, NMP and PEG. Variation of the bore liquid composition had a clear influence on the pure water flux and pore size (permporometry) (see Table 4). Open outside skins with relatively large pores could be realized when the air gap length was at least 10 mm. The pure water flux, BSA retention and pore size of various membranes as a function of the bore liquid composition are given in Table 4.

Table 4 clearly shows that with increasing pore size the pure water flux increases and the BSA retention drops. Adding PEG to the bore liquid increases the pore size and additional NMP even further increases the pore size. The higher the content of solvent in the bore liquid the larger the pores in the skin. When only water is used as bore liquid there will be a fast diffusion of water into the polymer solution and at a similar rate NMP and PEG will diffuse out of the dope solution into the bore liquid. Since the polymer solution has a composition close to the binodal composition only small amounts of extra water in the dope solution will cause phase separation; instantaneous demixing occurs, resulting in a rather dense skin layer with small pores.

When the content of solvent (NMP) and weak nonsolvent (PEG) in the bore liquid increase and at the same time the water content decreases diffusion of NMP and PEG out of the dope into the bore liquid will be reduced due to a smaller concentration difference. Mainly, water will diffuse into the dope solution, but at a slower rate than when 100% water was present in the bore. The initiated nuclei get the chance to grow before phase separation occurs. The longer the nuclei in the skin layer can grow the larger the pores become.

As discussed before the real pore size in the wet state might be different from the values reported in Table 4, which are measured in the dry state. To be able to measure a pore size with permporometry the fibers have to be dry. Even though a solvent replacement method (water by ethanol by hexane by air) was applied the smaller pores might still collapse or alter to some extend. However, a nice relationship was observed that with increasing pure water flux and decreasing BSA retention the measured pore size also increases.

SEM photographs (Fig. 5) have been taken of the inside and outside skin of the membranes corresponding to the membranes presented in Table 4. The photos clearly show a dense inside skin surface and an open shell side surface. From the photos it is hard to see the differences of the inside surface with varying bore liquid composition. What can be seen are a smooth surface when pure water is used and a rather rough surface when mixtures of $H_2O/NMP/PEG$ are used. When the pores of the inside surface increase it seems that the pores of the shell side surface become a little smaller and larger in number.

4.5. Pore size control of the shell side

For the production of hollow fiber membranes with the separation layer at the shell side a bore liquid



Fig. 5. SEM photographs of inside skin surface (left) and shell surface (right) of various hollow fiber membranes corresponding to the membranes presented in Table 4. Fibers are spun from dope E. (A) bore liquid = $H_2O/NMP/PEG$ (100/0/0), air gap = 10 mm; (B) bore liquid = $H_2O/NMP/PEG$ (70/0/30), air gap = 10 mm; (C) bore liquid = $H_2O/NMP/PEG$ (40/30/30), air gap = 10 mm; (D) bore liquid = $H_2O/NMP/PEG$ (26/37/37), air gap = 160 mm.



Fig. 6. SEM photographs of surface and cross-section of PES hollow fiber membranes as a function of the air gap length. Fibers are spun from dope E and corresponding to the fibers (batch no. 2) of Table 5. (A) bore surface (bore liquid 75/25 wt.% NMP/water); (B) cross-section bore side (bore liquid 75/25 wt.% NMP/water); (C) shell surface (air gap = 0 mm); (D) cross-section shell side (air gap = 0 mm); (E) shell surface (air gap = 10 mm); (F) cross-section shell side (air gap = 10 mm); (G) shell surface (air gap = 60 mm); (H) cross-section shell side (air gap = 60 mm).

Batch (no.)	Lumen composition		Air gap	Pure water flux	BSA retention	Pore diameter	SEM photo no.
	Water (wt.%)	NMP (wt.%)	(mm)	$(l/(m^2 h bar))$	(%)	(nm)	(Fig. 6)
1	15	85	0	562	100	8	
1	25	75	10	2150	56	54	A, B ^a
2	25	75	0	714	99	10	C, D
2	25	75	10	1826	73	40	E, F
2	25	75	60	1993	73	nm ^b	G, H

The effect of the air gap length on the pure water flux, BSA retention and pore size of various hollow fiber membranes prepared from spinning dope E

^a Bore structure of photos A and B are representative for all fibers of batch 2 with the same bore liquid composition of water/NMP (25/75).

^b nm: not measured.

composition with relatively high solvent content was chosen to create a rather open inside skin with relatively large pores (see also Fig. 6A and B). The pore size of the outside skin could be controlled to some extend by variation of the air gap length. The longer the air gap length the longer it takes before the outside skin phase separates. Instantaneous demixing occurs as soon as the nascent fiber enters the coagulation bath filled with water. During the residence time in the air the nascent fiber is penetrated by moisture from the air. Nuclei are formed and grow until phase separation arrest the structure when the fiber has entered the coagulation bath. The spinning solution had the same composition as solution E. In Table 5, the influence of the air gap length on pure water flux, pore size and BSA retention is presented.

The results clearly show that the pore size of the outside skin increases with increasing air gap length. Overall it can be concluded that the pure water fluxes are rather high. Again, a nice relationship was observed when increasing the air gap length the pore size increases, the BSA retention decreases and the pure water flux increases.

Fig. 6 shows the SEM photographs of the bore surface (6A) and bore side cross-section (6B) of the hollow fiber membranes of batch no. 2, which correspond to the last three fibers presented in Table 5. The SEM photographs, Fig. 6C–H show the shell surface and the shell cross-section of the same fibers. The bore surface and inside structures are very open and the pore size of the shell side surface increases with increasing air gap length as could be expected from the data presented in Table 5.

5. Conclusions

This study shows that PEG can be used very well as a polymeric additive to enhance the polymer (PES) dope viscosity and to enhance the pore interconnectivity, when added in appropriate amounts. A reduction in the T_g of the ultimate fiber from $T_g = 230 \text{ °C}$ (pure PES) to $T_g = 184 \text{ °C}$ is an indication that at least a part of the PEG 400 remains inside the fiber matrix and enhances its hydrophilicity.

A NMP/PEG ratio of 1:1 resulted in higher fluxes than a ratio of 1:4. The PES concentration did not have much influence on the pure water flux, which was purely controlled by the NMP/PEG ratio. Marcovoids were not suppressed by the addition of PEG alone. The molecular weight of PEG 400 was obviously too low. Therefore, additional nonsolvent (water) had to be added. When the amount of water was sufficiently high marcovoids could be suppressed and nice spongy structures were obtained.

Using a PES/NMP/PEG/water composition of 16/38.5/38.5/7 in (wt.%) asymmetric hollow fiber membranes with inside skin or outside (shell) skin could be produced with ultrafiltration properties. The pore size of the inside skin could be controlled well by varying the bore liquid composition, while the shell side pores were controlled by varying the air gap length. The pores of the shell side skin were larger than the pores created by varying the bore liquid composition. When the air gap exceeds a length of 10 mm the membranes produced show microfiltration like properties. The application of a solvent/nonsolvent mixture seems to be a more powerful parameter to

Table 5

influence the pore size than the air gap length. Therefore, a wet–wet spinning process using a triple layer spinneret is recommended for pore size and structure control of the shell surface.

The pore size of these hollow fibers was measured by permporometry and showed an excellent correlation with pure water flux and BSA retention. These fibers had to be dried by a solvent displacement method prior to permporometry analysis. Therefore, the true pore size might be somewhat different, since drying meso-porous membranes might very well alter the pore size and/or shape. Nevertheless, the procedure followed seems fair enough for comparison of relative values.

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