Micro- and Ultrafiltration Film Membranes from Poly(ether ether ketone) (PEEK)

MARK F. SONNENSCHEIN

Central Research and Development, The Dow Chemical Co., Midland, Michigan 48674

ABSTRACT: Film membranes from the thermoplastic poly(ether ether ketone) (PEEK) have been extruded and tested for their microfiltration and ultrafiltration performance. High-performance asymmetric membranes have been obtained by extruding polymer blends of PEEK, polysulphone, and a small molecule solvent mixture, and then by removing the polysulphone and solvent in a subsequent extraction step. The process for making ultrafiltration membranes differs from microfiltration membranes only in the relative blend components, and the temperature of the film pick-up rolls. Processing parameters with important effects on the membrane performance have been identified. Microfiltration membranes are characterized by their pore-size distributions and SEM, and ultrafiltration membranes by their rejection of bovine serum albumin, bubble point, and SEM. Composite membrane for nanofiltration utilizing the PEEK ultrafiltration membrane as a substrate performed similarly to a commercial membrane for the same purpose. This work details the best method for making PEEK film membranes published to date. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1146–1155, 1999

Key words: microfiltration; ultrafiltration; PEEK; poly(ether ether ketone); membrane

INTRODUCTION

A wide variety of polymeric materials are commonly used for making membranes.[1] Current polymer membrane materials are practical for low-temperature aqueous separations. More demanding separations have generally required the use of ceramic membranes, although these are far more expensive and difficult to make than polymeric membranes.[2] The class of semicrystalline materials, including poly(ether ether ketone) (PEEK)[3–7] and poly(phenylene sulfide) (PPS),[8–10] are materials that should provide many of the capabilities of ceramic membranes in terms of temperature and solvent resistance, although allowing the relatively easier processing and fabrication of polymer membranes.

Many polymeric materials are easily processed into membranes using the thermally induced phase inversion process (TIPS).[11] TIPS refers to the method whereby the polymer is dissolved in a solvent in which the solubility of the polymer in the solvent is temperature dependent. The polymer solvent blend is extruded or cast at one temperature, and as the temperature proceeds to ambient, the polymer phase separates from the solvent.[11–13] The solvent is subsequently removed from the phase-separated blend in a leach step. The sites in the polymer vacated by the solvent then act as conduits for the flow of liquids. A procedure for extrusion of hollow fiber microfiltration membranes from PEEK employing the TIPS method was described in a previous publication.[14] Extrusion of film microfiltration (MF) membranes from PEEK requires substantially different considerations than fibers and is the subject of this article.

Modern techniques for forming ultrafiltration (UF) membranes often employ the solvent inversion process. The solvent inversion involves the casting or extrusion of the polymer/solvent blend into an exchange bath that exchanges freely and rapidly with the membrane polymer solvent and is a nonsolvent for the polymer. This technique, when properly controlled, will result in an asymmetric membrane with a very tight pore structure on the surface and a much more open porous structure within the membrane bulk. Such a structure is usually required for the molecular weight discrimination ultrafiltration applications require. Because of the very high temperatures at which PEEK membranes are extruded in the TIPS method, we have found that PEEK microfiltration and ultrafiltration membranes can both be formed using the TIPS method with pore size distribution and membrane isotropy strongly dependent on process conditions. This article will present procedures for extrusion of asymmetric microfiltration and ultrafiltration film membranes from PEEK using the TIPS method. The only distinction between the process for making micro- and ultrafiltration membranes is the blend composition and the temperature of the rolls onto which the film is extruded.

EXPERIMENTAL

PEEK 450G (T_g, $\sim$ 150°C; T_m, 335°C) was obtained from Victrex Corporation (West Deptford, NJ) under the trade name Victrex. Polysulphone (PS) was obtained from Amoco Plastics under the trade name Udel-3703 (T_g, $\sim$ 190°C). A blend of 75% diphenylisophthalate (DPIP) (T_m, 137; bp, 390°C)/25% diphenylterephthalate (DPTP) (mp, 197°C; bp, 410°C) was obtained from Hoechst Celanese (Charlotte, NC). DPTP and DPIP were purchased separately from Sloss Industries (Birmingham, AL). Di-phenyl phthalate esters are high-temperature solvents for PEEK with low vapor pressures under typical extrusion conditions. Their mixture also provides a blend that recrystallizes very slowly allowing the extruded product to be rolled on a collection device after extrusion without cracking. HB-40 (bp, 390°C) is a product from Monsanto Corporation that is a blend of hydrogenated terphenyls. We have observed that HB-40 helps maintain film flexibility after extrusion and provides membranes with pore-size distributions at smaller sizes. All materials were used as received.

Table I   Extruder and Process Variables for PEEK Film Membrane Extrusion

Zone	Temperature (°C)
Feed throat	250
Zone 1	330
Zone 2	305
Zone 3	300
Zone 4	300
Transition	300
Pump block	300
Pack well	310
Die adaptor	310
6 or 8-in. Die	310
12-in. Die	320
Film pick-up roll	60–200

Feed rates: 40–100 g/min, linear extrusion rates: 4–20 ft/min.

Polymer solutions were obtained by first blending the DPIP/DPTP and HB-40 with the PS in a closed resin kettle until the mixture was a homogeneous, transparent, amber color, occurring around 200°C. PEEK was then added in small increments and the mixture was heated to 340°C to assure uniform blending. The resin kettle temperature was controlled using an Omron temperature controller connected to a thermocouple submerged in the blend. The polymer blend was mixed using moderate shear mixing blades attached to an air-driven motor. When the PEEK is fully mixed into the solution, the blend is dark brown and transparent (when observed through a small pathlength). The blend is then carefully poured from the kettle into a metal pan, covered, and allowed to cool quiescently. The light brown PEEK/PS/DPIP/DPTP/HB-40 blend was then chipped in an IMS Co. grinder to a size suitable for feeding to an extruder.

Films were extruded on a 0.8-in. Welding Engineers twin-screw extruder with counter-rotating nonintermeshing screws, or on a 1-in. Killion single-screw extruder. In both cases, the melted polymer blend was metered to the film die with a 1.78 g/rev Zenith melt pump. Films were extruded through Killion sheet dies for 6 or 8-in. wide films or an EDI 12-in. die deckled to a 10-in. width. The melt was filtered through a screen pack with 80 and 200 mesh screens. Extruder discharge pressures were generally below 300 psi, and pump suction pressures were maintained at 100 psi. Extruder temperature profiles for representative polymer blends are provided in Table I.

The high initial temperature is used to ensure complete melting of the PEEK blend, and the lower temperatures in zones 2 through the pump block provide sufficient viscosity that a screw suction pressure is maintained. Films were extruded to a Killion temperature-controlled film pick-up connected to a Sterlco heater. The distance from the die lips to the godet surface was 5 mm. Films were wound on a Killion tension-controlled film take-up in most experiments.

Removal of the PS and solvent from the extruded film (leaving a PEEK membrane) was accomplished by leaching in methylene chloride baths. The extent of leaching was followed by the addition of ethanol to an aliquot from the leach bath. This method is very sensitive to the presence of PS and phthalate esters, turning the solution cloudy when ethanol is added. Leaching was conducted until an aliquot of the leach bath no longer turned cloudy on addition of ethanol. Scanning electron micrographs (SEM) indicate no observable PS or phthalate remain in the membrane when this test is applied (residuals would appear as globular, spherical, or platy features in the micrographs).

When no PS or phthalate ester was observable in the methylene chloride bath, the methylene chloride was displaced by submersion of the membranes into a 95% ethanol or isopropyl alcohol bath. Membrane drying was accomplished by rerolling the IPA saturated membrane onto a roll interleaving the membrane wraps with an absorbent paper towel. This allows the membrane to dry with minimal change in volume and eliminates sticking of the membrane to previous wraps.

Membrane porosity was tested by punching film samples of specific geometry and averaging the film thickness over 12 locations. Porosity was then determined by application of eq. 1

$$P_{\text{sample}} = 1 - (\rho_{\text{sample}}/\rho_{\text{dense}}) \tag{1}$$

In eq. 1, P is the sample porosity, ρ_{sample} is the measured density of the sample, and ρ_{dense} is the density of nonporous semicrystalline PEEK. ρ_{dense} is calculated from the average crystallinity of the samples (calculated from DSC data) and the known[15] densities of amorphous and crystalline PEEK (amorphous = 1.2626 g/mL; crystalline = 1.4006 g/mL) and by using a theoretical heat of fusion of 100% crystalline PEEK of 130 J/g.[16]

Membrane-pure water permeability was determined by mounting the membrane in a Microfiltration Systems (Dublin, CA) test cell, or a stainless steel test cell for high-pressure testing and wetting with ethanol. From this condition, a bubble point test may be performed to determine maximum and mean pore sizes.[17] Our experiments showed with remarkable consistency that the mean pore size was 0.5 ± 0.1 of the maximum pore size. Alternatively, from the ethanol-saturated state, the ethanol can be exchanged with water to determine the pure-water flux. Pure-water microfiltration transmission rates were performed at between 2 and 5 psi transmembrane pressure, whereas UF pure-water transmission rates were performed at 20 psi.

Protein rejection experiments were performed using an Amicon UHP-43 test cell and 11.5-cm^2 membrane surface area. The membrane was prewetted by permeating ethanol through the membrane followed by extensive washing with deionized water. The test involved filtering 25 mL of deionized water, followed by filtering 12.5 mL of a buffered 0.25% bovine serum albumin (BSA) solution, followed by taking 25 mL of permeate from a 0.5% BSA solution. BSA has a reported molecular weight of 66,000 a.m.u. and is reported to have a 4×14 nm elliptical configuration.[18] Test pressure was 55 psi. Rejection was monitored by ultraviolet absorption following treatment of the permeate by an indicator[19] (BCA Protein Assay Reagent, Pierce Chemical).

Nanofiltration membranes were prepared using PEEK UF membrane substrates with a maximum pore size of 17 nm and a pure-water flux of 300 mL/(m$^2 \times$ h $\times$ cmHg) by using the procedure of Cadotte.[20] The PEEK UF membranes were initially wet with a 50/50 mixture of isopropyl alcohol and deionized water. The alcohol mixture was then displaced with deionized water. The PEEK UF membranes were then soaked in a fresh 4% solution of m-phenylene diamine for 20 min. The samples were then removed and blotted of excess diamine and quickly plunged into a 0.4% solution of trimesyl chloride in Isopar L. After 3 min the samples were removed and placed in deionized water for 20 min and subsequently submerged into a separate beaker filled with hot deionized water. After 20 min the discs were removed, dipped into a solution of 2% polyvinyl alcohol, and then air dried for 24 h. The membranes were then placed into test cells and rewet with 50/50 isopropyl alcohol/water that was subsequently displaced with circulating 2000 ppm NaCl at 250 psi.
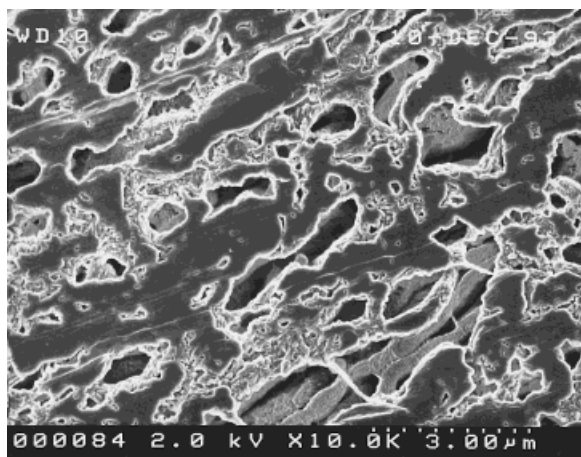
(a)
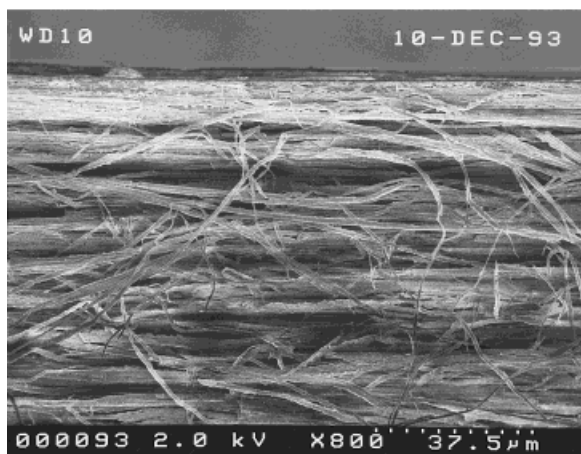
(b)

Figure 1 Scanning electron micrographs of a PEEK film membrane from a blend containing 30 wt % polysulphone. (a) Surface; (b) cross section.

Permeate salt concentration of these membranes was tested using a calibrated conductance bridge and compared to a commercial membrane made by Filmtec Corporation.

RESULTS AND DISCUSSION

A variety of PEEK blend compositions were tested for their applicability in making film membranes. Unlike PEEK hollow-fiber membranes that were optimal with 30% PS in the blend,[14] such blends did not result in good film membranes. Membranes with PS content > 20 wt % were directional in their properties exhibiting

very low tear strength in the extrusion direction. Electron micrographs of these membranes reveal the origin of this effect (Fig. 1). Below 20 wt % PS, the directionality of the extruded membrane was no longer visible. The directionality is ostensibly due to a low extruder die temperature causing extensive phase separation within the extruder (i.e., prior to exiting the film die). These macrophase-separated regions under shear from the film die, followed by a rapid quench by the film take-off rolls, do not allow the PEEK blend film to relax its orientation prior to solidification. PEEK blends containing <20% PS, although phase separated prior to exiting the film die, were of sufficiently low viscosity to allow the extruding membrane to relax at least some of its orientation prior to solidification. The quench rate of film extrusion relative to fiber extrusion also seems to play a role in the morphological differences. By observation, from the die lips to the relatively cool pick-up rolls, the film is quenched from the molten state to solid state in approximately 0.5 s. Quenching is marked in this observation by the ability to remove the extruded blend from the roll surface without changing the product's dimensions. In contrast, it is estimated that the molten hollow-fiber membrane is at an elevated temperature for approximately 5 s[14] because it is large (1.5-mm OD, 1-mm ID) and touches the godet rolls only tangentially. During those 5 s, the molten fiber is able to undergo extensive phase separation, relaxation of orientation, and growth of nucleated polymer crystals.[21] On the other hand, the molten films, allowed just 0.5 s prior to quench, are unable to achieve the same state. The poor mechanical properties of films containing in excess of 20% PS are due to the short time allowed for relaxation of orientation coupled with the
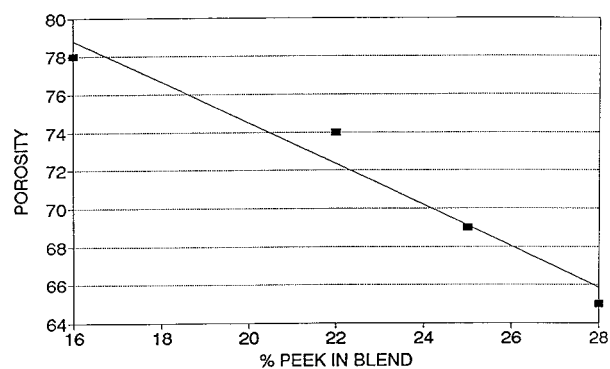

Figure 2 Membrane porosity as a function of PEEK content for blends containing 16 wt % polysulphone.
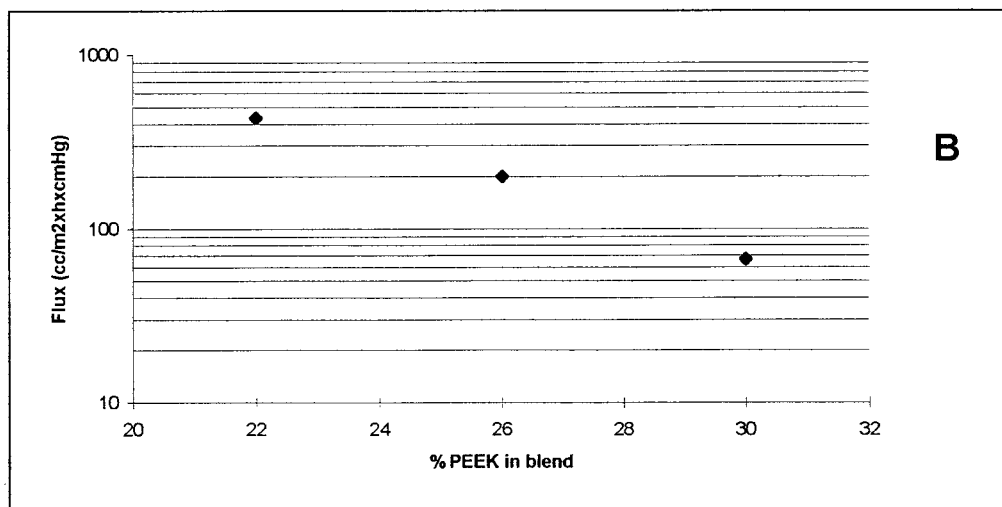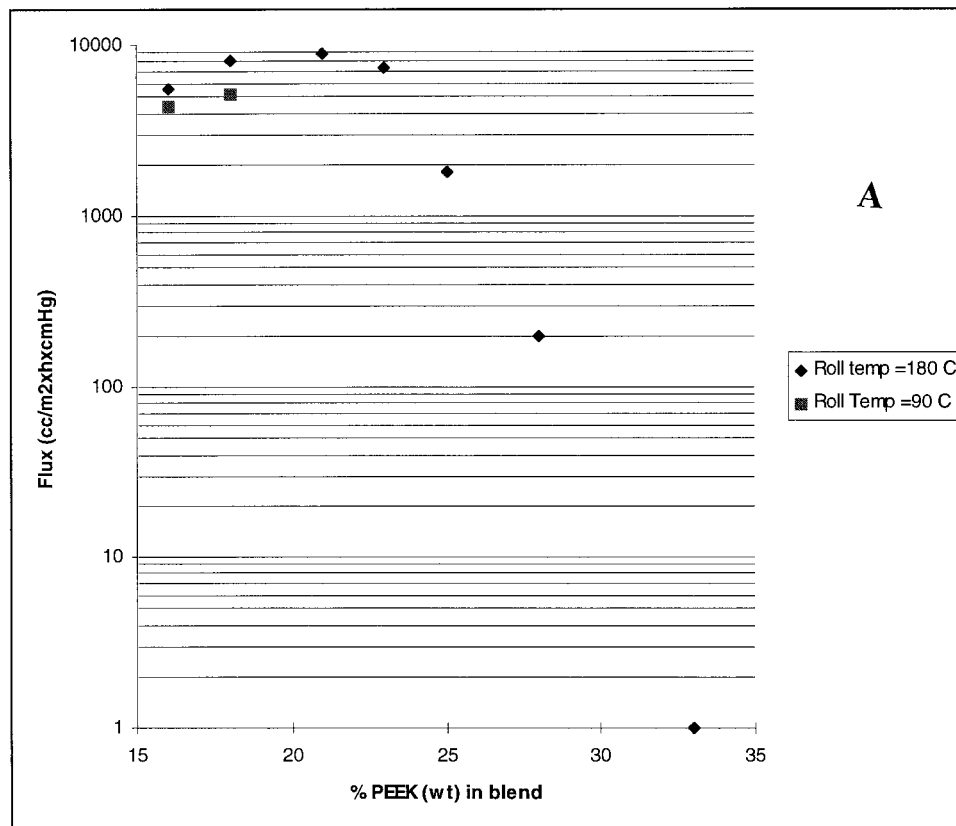
Figure 3   Pure-water flux for PEEK membranes extruded from blends containing (A) 16 wt % polysulphone (microfiltration), and (B) 7 wt % polysulphone (ultrafiltration). Film pick-up roll temperatures are 180°C except where noted.

high-blend viscosities further slowing down the relaxation kinetics. Furthermore, it has been reported that PEEK compatible polymers such as PS slow and even hinder PEEK crystallization.[22–24] Thus, the improved film membranes obtained with low PS content blends result from balancing blend viscosity with blend-phase separation kinetics and PEEK crystallization.

Membrane porosity is one of the fundamental measures of a membrane's performance.[25] Previ-
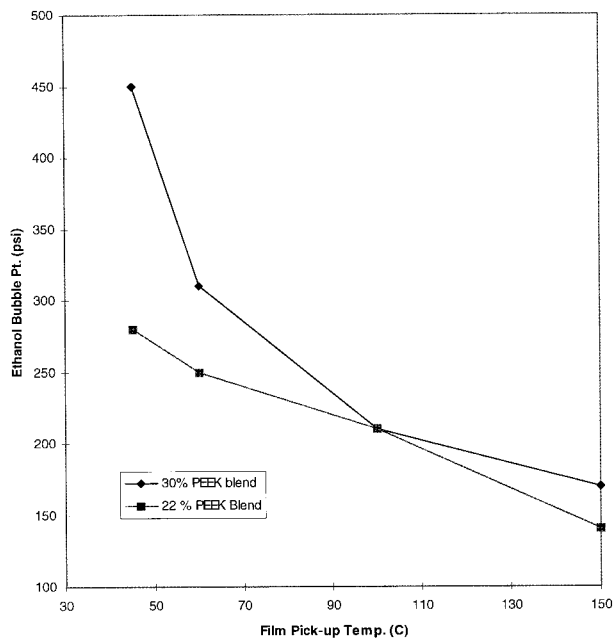
Figure 4 Ethanol bubble point versus film pick-up roll temperature for blends consisting of 22% PEEK, 12% PS, 10% HB-40, 56% DPIP/DPTP and 30% PEEK, 7% PS, 10% HB-40, and 53% DPIP/DPTP. Maximum pore size for an ethanol bubble point from the ratio 9.25/bubble point (psi).

ous experience has led to the conclusion that PEEK membrane porosity was generally 5% less than that calculated based on PEEK weight percentage in blend.[14] This trend is further documented for higher porosity PEEK membranes in Figure 2. Although it is tempting to postulate a straight line dependence, such an assumption is not warranted. The flattening of the porosity versus concentration data from 22 to 16% PEEK is continued by an experiment-making membrane from a 14% PEEK and 18% PS blend that yielded a porosity of 79% (this point is not plotted because of the different PS content).

Figure 3(A, B) shows PEEK film membrane performance from blends that result in MF and UF membranes, respectively, as a function of PEEK concentration. The result that decreasing PEEK concentration < 18% (weight) results in an unchanged or slightly lower pure water flux suggests that other experimental parameters are exerting a substantial influence on the phase-separation process. One such important effect on membrane flux is indicated on Figure 3(A) as the film roll pick-up temperature. The preferred process described in this work utilizes heated pick-up rolls, and the temperature of the rolls may in

some cases have a substantial effect on the resulting membrane as seen in Figure 4. This effect results from increasing the phase separation time of the extruding blend resulting in the pore size distribution moving to larger sizes.[26] Although no attempt has been made to explicitly determine the kinetics of phase separation in these systems, the strong dependence of roll temperature on membrane performance at higher PEEK concentration suggests that Ostwald ripening and coalescence are mechanisms in the membrane formation. The decreasing influence of temperature at lower PEEK concentrations shown in Figure 3(A) suggests that the phase-separation mechanism may be more strongly influenced by hydrodynamic flow which is independent of phase separation temperature.[27]

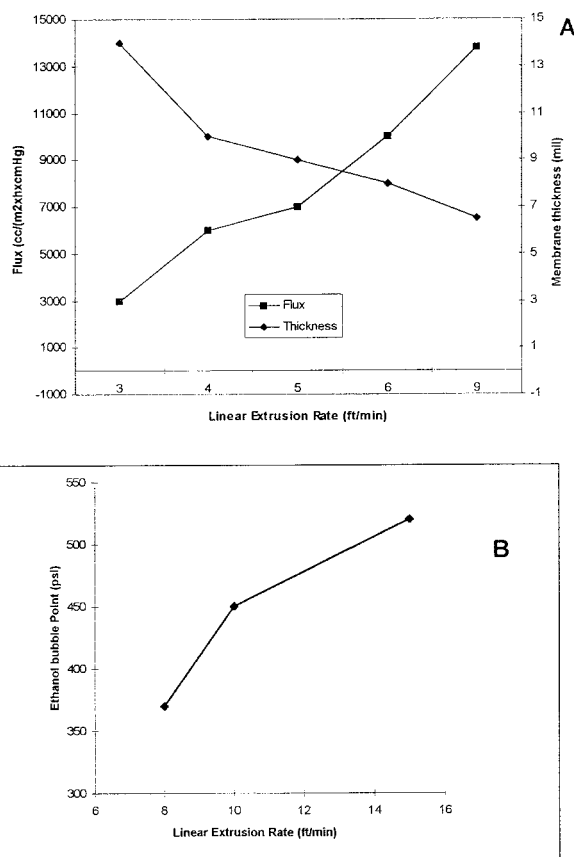Another important parameter affecting PEEK film membrane performance is the film pick-up

Figure 5 Relationship between membrane-pure water flux, membrane thickness, and linear extrusion rate for membrane containing (A) 20% PEEK, 16% polysulphone, 10% HB-40, and (B) 30% PEEK, 7% PPS, 10% HB-40. Pick-up roll temperatures were 180°C for this experiment.

Table II Effect of Postextrusion Processing Conditions on Membrane Performance from 14% PEEK/ 18% PS/63% DPIP/DPTP Blend/5% HB-40 Polymer Blend

Film	Drying Condition	Flux (cc/m^2 $\times$ h $\times$ cmHg)	Maximum Pore Size (μm)	Comments
1	a,d	1700	0.11	brittle, brown, curled
2	b,d	3200	0.15	brown, curled
3	b,e	4400	0.15	white, flexible, thin
4	c,e	4200	0.15	white, flexible, thin
5	c,f	13,500	0.21	white, flexible, thin

(a) From methylene chloride; (b) from isopropyl alcohol; (c) from ethanol; (d) dried without constraint; (e) dried under high uniaxial tension; (f) dried under moderate tension.

Flux conversion: 0.003 gfd/psi = 1 cc/m^2 $\times$ h $\times$ cmHg; 1 gfd/psi = 25 L/m^2 $\times$ h $\times$ bar.

speed. In general, it is viewed as desirable to maximize roll speed to increase the productivity of the extrusion.[28] As mentioned previously, however, the relationship between roll speed and membrane performance is complicated. Simply increasing the roll speed decreases the film residence in the gap between the die lips and the film pick-up rolls, but it also increases the polymer orientation and decreases the membrane thickness. One can imagine many effects that can occur as a result of these changes, and these effects could be mutually dependent. For instance, increasing the membrane orientation may elongate the pores, and doing so, increase the size of some pores while closing up others completely. Similarly, decreasing the membrane's thickness (a result of increasing the linear extrusion rate at constant mass flow), should, all other things being equal, increase the membrane flux. But if the effect of the thinner membrane is to increase the overall quench rate of the membrane, the flux may be smaller because of the pore size distribution moving to smaller sizes.[29]

The membranes formed by PEEK blends explored in this study fell into two classes with respect to the effect of film pick-up roll rate. For those membranes of which performance could be described as microfiltration (maximum pore size > 0.05 μm), it was observed that increasing the film take-up speed had the effect of increasing the membrane flux with insignificant change in maximum and mean pore size [Fig. 5(A)]. For those blends producing membranes that could be described as UF (maximum pore size < 0.05 μm), the increased take-up rate had the effect of decreasing the maximum pore size with insignificant change in flux [Fig. 5(B)].

Another important factor affecting the membrane performance was the effect of solvent exchange on membrane properties. When employing a leaching solvent such as methylene chloride, it is common to displace the methylene chloride with another solvent for the drying step.[30] This is done to allow slower drying and easier handling. We have observed that using alcohol (isopropyl or ethanol) followed by an exchange with water results in membranes that are deformed by wrinkles and have very low water permeability. We surmise that this is a result of the nonsolvent nature of water for PEEK. PEEK absorbs methylene chloride and ethanol up to 10 and 4 wt %, respectively, at room temperature.[31,32] When alcohol is rapidly displaced by water, those areas in immediate contact with water will shrink in an attempt to reduce residual stress. This shrinkage is sometimes as much as 30% in the extrusion direction. In fact, this shrinkage is much faster than a worker's ability to place the film in a geometry-constraining device. On the other hand, when the methylene chloride is exchanged with 95% ethanol or isopropyl alcohol, the shrinkage is much less and the film does not deform. This phenomenon is presumably due to the ability of alcohols to swell PEEK and the relative inability of water to do the same (<0.1 wt %).

The tension under which the membrane dries also has an important effect on the ultimate membrane properties. We do not have the capability to quantify the effect; nevertheless, the result is unmistakable. When dried without constraint, the membrane curls and significant flux is lost. When dried under strong tension (tension just below the film tear strength) in the extrusion direction, the membrane does not curl, but flux loss up to 80% is observed. When the film is rolled with tension sufficient only to prevent accidental folding of the membrane, membrane width is maintained and the flux is maximal. Table II contains qualitative
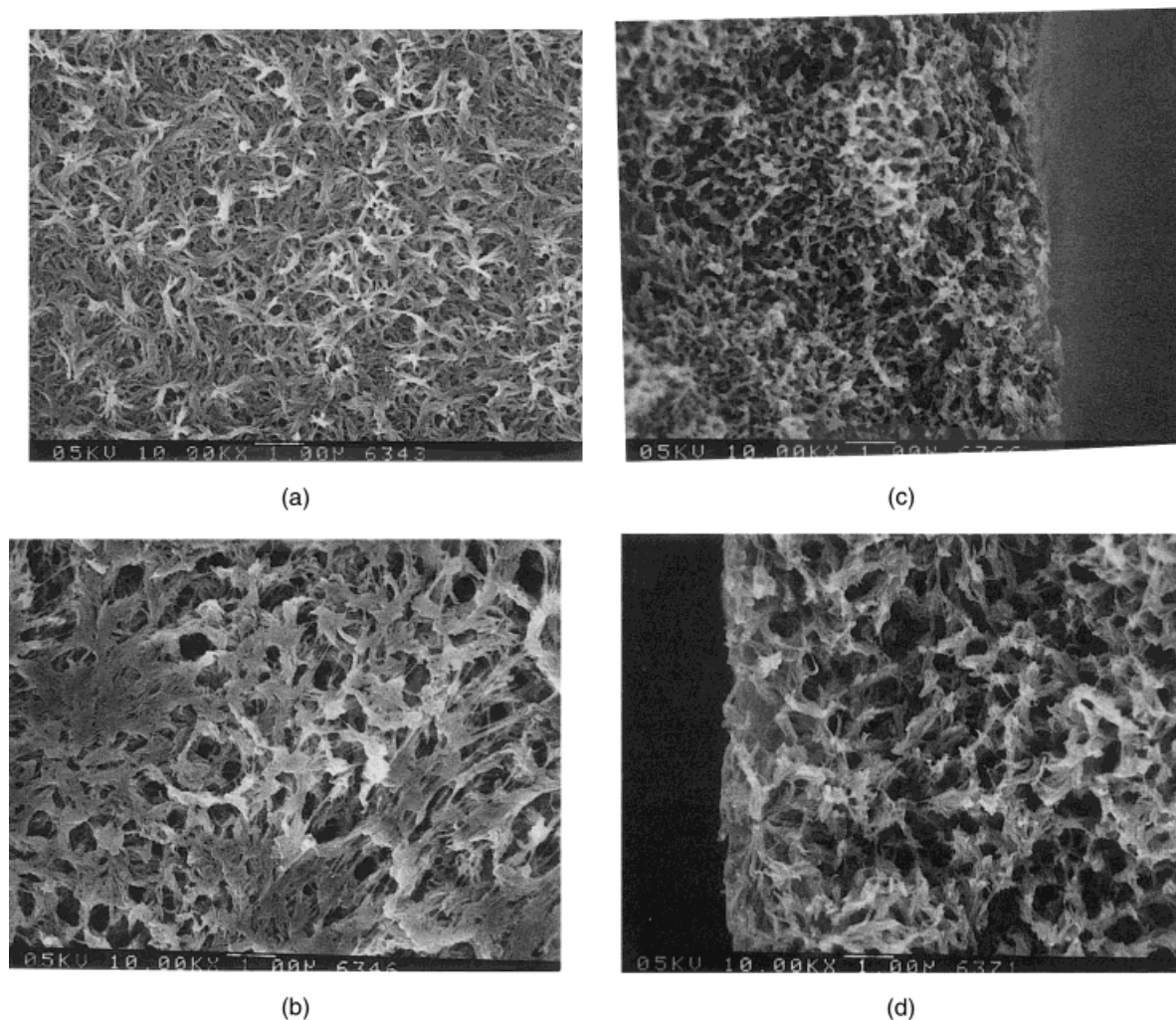
Figure 6 Scanning electron micrograph of a PEEK film membrane from a blend consisting of 14% PEEK, 18% PS, 5% HB-40, 63% DPIP/DPTP. (A) Surface of film pick-up contacting side, (B) surface of air-contacting side, (C) cross section of film directly beneath film pick-up contacting surface, (D) cross section of film directly beneath air contacting surface.

information relating our experience in the relationship between postextrusion-processing conditions and membrane properties.

The membranes produced by the methods described here possess morphologies that may be considered conventional for polymer membranes.[33–35] The microfiltration membranes (Fig. 6) possess PEEK structures that are consistent with the extrusion of a cocontinuous structure with the PS component existing in a broad distribution of domain sizes prior to leaching. The membrane surface that first contacts the film pick-up roll during extrusion quenches slightly more quickly, and this difference is reflected in a greater population of small pores directly under the surface and on the

surface. The UF membranes (Fig. 7) obtained through our thermal inversion process possess different structures than those usually observed from the solvent inversion process (SIP).[36] Without the rapid displacement of the extractable phase for a fluid phase, the membranes exhibit no finger structures often observed via SIP. Many UF membranes using the SIP are produced by deposition on one side of a MF substrate.[37] This procedure can also allow the membrane to possess highly asymmetric surfaces that are beneficial in some applications. Although the PEEK UF membranes produced by the TIPS also possess asymmetry by virtue of the differential quench applied to the extruding film, the degree of asymmetry is apparently much less
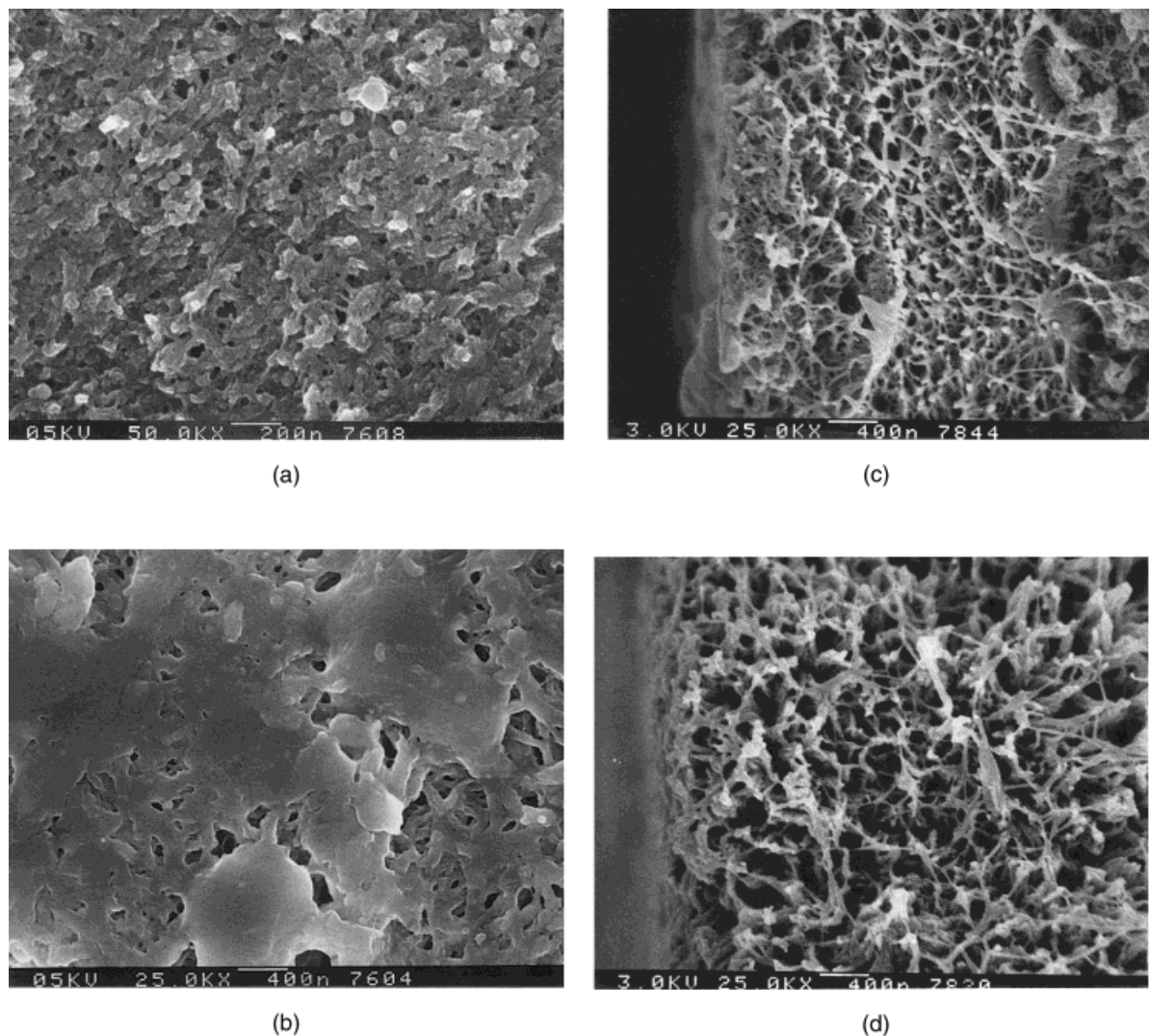
Figure 7 Scanning electron micrograph of PEEK ultrafiltration membrane from a blend consisting of 30% PEEK, 7% PS, 10% HB-40, and 53% DPIP/DPTP. (A) Film pick-up contacting surface, (B) air contacting side, (C) cross section directly beneath film pick-up contacting surface, (D) cross sectional view directly beneath air contacting surface.

than can be obtained via SIP.[38] Despite this, our membranes with a bubble point of 540 psi (17 nm maximum pore size) passed the BSA rejection test, rejecting >99.9%. This was done losing only 12% of the pure-water permeability, suggesting that fouling of the membrane by the protein was not an important effect.[19] These PEEK membranes, therefore, represent an unusual example of highly performing UF membrane formation employing a continuous process via TIPS. This is allowed by our ability to produce a relatively tight surface pore structure on the roll-contacting side during the extrusion. Reverse-osmosis composite membranes prepared using PEEK UF membranes in this study provided a salt passage of 2.6% (±1.2%) at a water flux of 28 gallons/(sq ft × day) compared to a salt passage of 1.6% at 26 gallons/(sq ft × day) of the commercial reverse-osmosis membrane.

Although the MF membranes produced in these studies possess performance levels within the range of commercially available film membranes from other polymers, the UF membranes suffer from relatively low permeability rates. The reasons for this are first, the relatively high density of the membrane due to relatively low asymmetry, and second, insufficient porosity on the surface. Given the data

provided in this study, a possible route to achieving greater asymmetry and a greater transmembrane flux is to move the film pick-up rolls closer to the die lips, actively cool the film pick-up roll to lower temperatures than achieved in these experiments, and at the same time, reduce the PEEK and PS content in the blend.

CONCLUSIONS

This article provides procedures for obtaining film membranes from PEEK with micro- and ultrafiltration performance. The membranes are obtained using blends of PEEK, PS, and a small molecule solvent mixture. The membranes are formed through a thermal inversion process requiring an extruder and temperature-controlled film pick-up rolls. Important parameters affecting membrane performance are the blend composition, the temperature of the film pick-up rolls, the linear extrusion rate, the film-leaching conditions, and the film-drying conditions. Membrane morphologies are asymmetric because of the differential thermal quench applied to the extruding film when contacting the pick-up rolls.

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