

Characteristics of Poly(ether ether ketone) Microporous Membranes Prepared via Thermally Induced Phase Separation (TIPS)

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ABSTRACT: The morphology and bulk properties of microporous membranes based on poly(ether ether ketone) (PEEK) have been investigated as a function of initial casting composition and thermal and mechanical processing history. Membranes were prepared via solid-liquid phase separation of miscible blends of PEEK and polyetherimide (PEI), with subsequent extraction of the PEI diluent. Scanning electron microscopy studies revealed a microporous morphology with two distinct pore size scales corresponding to diluent extraction from interfibrillar and interspherulitic regions, respectively. The membrane structure was sensitive to both initial blend composition and crystallization temperature, with the resulting pore size distribution reflecting the kinetics of phase separation. For membranes prepared with lower initial diluent content or at lower crystallization temperatures, mercury intrusion porosimetry indicated a relatively narrow distribution of fine interfibrillar pores, with an average pore size of approximately 0.04 microns. Membranes prepared at higher diluent content or at higher crystallization temperatures displayed a broad pore distribution, with a sizeable population of coarse, interspherulitic pores (0.1 to 1 μm in size). Uniaxial drawing led to a fibrillated network structure with markedly higher water flux characteristics compared to the as-cast membranes. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2347-2355, 1997

Key words: poly(ether ether ketone); membranes; thermally induced phase separation

INTRODUCTION:

The development of thermally resistant microporous membranes from semicrystalline engineering thermoplastics is a subject of considerable interest. For many semicrystalline thermoplastics, membrane fabrication using conventional solvent-based methods is not possible, owing to

the chemical intractability of the materials involved. The thermally induced phase separation (TIPS) approach, however, has been shown to be an effective and versatile technique for the preparation of microporous membranes based on polyolefins and advanced engineering thermoplastics such as poly(ether ether ketone) (PEEK) and poly(phenylene sulfide) (PPS).¹⁻¹⁴ In the TIPS method, the polymer of interest is blended with a high-boiling diluent at elevated temperature such that a homogeneous melt is formed. The mixture is then cooled, leading to solid-liquid or liquid-liquid phase separation and eventual solidification; selective extraction of the diluent provides

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the desired microporous article. The TIPS approach is particularly advantageous for the generation of isotropic membrane structures.

Two recent patents detail the application of the TIPS method for the fabrication of microporous hollow fibers from PEEK.^{15,16} Although an extensive list of suitable low molecular weight diluents was reported,¹⁷ a persistent difficulty encountered in processing was the low viscosity of the casting mixture at the high temperatures required to obtain a single-phase melt. One remedy proposed for this problem was the introduction of a second, amorphous polymer (e.g., polysulfone) in the melt mixture to increase the viscosity. The primary drawback of this approach was that the second polymer was only partially miscible in the blend mixture, thus complicating the casting system and rendering the control of membrane morphology more difficult.

In this article we examine the structure and bulk characteristics of a series of membranes based on blends of PEEK with polyetherimide (PEI). PEI is an amorphous engineering thermoplastic that displays a high glass transition temperature and excellent toughness; unlike PEEK, PEI is soluble in a number of common solvents. PEI is melt miscible with PEEK at all compositions,¹⁸ and thus is as an appropriate diluent for membrane fabrication via the TIPS method. By using a polymeric diluent, the processing difficulties associated with low molecular weight diluents can be avoided.

The solid-liquid phase separation characteristics of the PEEK/PEI blends have been investigated in detail by microscopy and thermal analysis methods.¹⁹⁻²² As PEEK crystallizes from the blend, three potential morphologies may be observed that reflect the nature of PEI exclusion from the evolving crystallites: interlamellar, interfibrillar, and interspherulitic. For conditions at which the rate of crystallization is fast relative to the rate of PEI diffusion, the interlamellar morphology may dominate, while at conditions where the rate of crystallization is slow relative to the rate of PEI diffusion, interfibrillar or interspherulitic morphologies are favored. Dielectric and dynamic mechanical studies of crystallized PEEK/PEI blends indicated the coexistence of a mixed interlamellar phase and a pure PEI interfibrillar/interspherulitic phase for all compositions and crystallization conditions examined.^{22,23}

In a previous publication,²³ we described the structure of PEEK/PEI membranes prepared via

the TIPS method. Exposure to liquid dichloromethane resulted in the extraction of the PEI diluent from interfibrillar and interspherulitic regions, thus providing porosity in the final article; PEI trapped between crystal lamellae (i.e., in the interlamellar phase) was retained in the membrane, leading to an enhancement in its thermal resistance properties. Two extraction size scales were observed in the resulting membranes: extraction from between fibrils led to fine pores, while extraction from interspherulitic pockets produced relatively coarse pores. The population of coarse pores increased with increasing PEI content in the initial blend.

The work reported here concerns morphological aspects of the PEEK/PEI membranes as a function of composition and thermal and mechanical processing history. Scanning electron microscopy, mercury intrusion porosimetry, and water flux measurements were carried out in an effort to elucidate the structural characteristics of these materials. The studies indicated considerable sensitivity to initial composition and to the processing temperature used to induce solid-liquid phase separation: lower crystallization temperatures led to a tighter morphology with fewer interspherulitic pockets. Postprocess drawing of the membranes produced a highly fibrillated structure comprised of a network of microfibrils radiating from the individual spherulites. The water permeability of these drawn membranes was markedly higher than that measured for the as-cast material.

MATERIALS AND EXPERIMENTAL METHODS

PEEK (Victrex 450G) was obtained in pellet form from Victrex U.S.A., Inc., West Chester, PA. PEI pellets (Ultem 1000) were obtained through the courtesy of GE Plastics, Mount Vernon, IN. All materials were dried under vacuum prior to use. PEEK/PEI blends encompassing a range of compositions were prepared by melt extrusion of tumbled pellet mixtures in a Custom Scientific Instruments (CSI 194) mixing extruder at 370°C with pelletization of the resulting blend strands.

Membrane precursors were prepared in the form of films measuring 40 × 40 × 0.10 mm. Blend pellets were compression molded in the melt with subsequent quenching in ice water (for cold crystallization studies) or direct transfer to a second

press for isothermal (melt) crystallization. Cold crystallization of the quenched amorphous films was carried out in the temperature-controlled press for 3 h at temperatures of 260, 280, and 300°C. Melt crystallizations were carried out for 1 h at 260 and 300°C. Extraction of the PEI diluent from the crystallized blend films was accomplished by immersion in liquid dichloromethane at 25°C. The extracted membranes were then transferred to 100% ethanol to minimize shrinkage. Solvent was removed by drying in a dynamically evacuated oven (10 Pa) at 25°C (first 100 h) and then at 100°C.

Scanning electron micrographs of the membrane surface and cross-sections were obtained using Hitachi S-2300 and S-2700 microscopes; all samples were coated with gold-palladium alloy prior to examination. The accelerating voltage was 25 kV. Cross-sectioned samples were prepared by fracturing in liquid nitrogen.

Mercury intrusion porosimetry studies were performed using an Autoscan 60 porosimeter from Quantachrome Corporation, Boynton Beach, FL. Samples were cut into thin strips (3 × 20 mm) and dried under vacuum at 100°C prior to examination. Cumulative mercury intrusion volume was measured at pressures up to 2000 bars.

The pure water flux characteristics of both as-cast and drawn membranes were measured using a homebuilt dead-end filtration cell with pressurization provided by nitrogen gas; applied pressures of 3.8 bars (55 psi; as-cast membranes) and 1.4 bars (20 psi; drawn membranes) were used. Each experiment was carried out for 90 min to ensure steady-state flux values. The reported data represent an average of three separate experiments for each membrane type, with an observed variance of less than 10%.

RESULTS AND DISCUSSION

The morphology of the extracted PEEK/PEI blends was investigated as a function of thermal history for both cold-crystallized and melt-crystallized samples. In Figure 1, scanning electron micrographs are shown for extracted membranes based on an initial blend composition of 25/75 PEEK/PEI. These materials were prepared by compression molding at 400°C, with quenching in ice water. The amorphous films were then isothermally cold crystallized at either 260, 280, or 300°C for 3 h, and subsequently extracted with liquid

dichloromethane. The micrographs in Figure 1 show the surface of these membranes.

The segregation of PEI in the blends during solid-liquid phase separation is controlled by the kinetics of PEEK crystallization relative to the diffusion of the PEI diluent. The lowest crystallization temperature examined, 260°C, corresponds to the highest crystallization rate observed for this blend composition. Under these conditions, PEI is trapped primarily in interlamellar and interfibrillar regions, with little interspherulitic segregation. In Figure 1(a) ($T_c = 260^\circ\text{C}$), densely packed spherulites are evident, with a relatively small population of interspherulitic pores distributed over the membrane surface. At higher crystallization temperatures (lower crystallization rates), the PEI is segregated over longer length scales, with a greater degree of interspherulitic exclusion. This is evident in Figure 1(b,c) ($T_c = 280$ and 300°C), where large pores and a much higher degree of surface porosity are observed upon extraction of the PEI diluent.

In addition to the crystallization temperature, the presence of nucleating agents can have a significant effect on the morphology of TIPS-based membranes.^{9,12,14,24-27} Heterogeneous nucleation sites are often present in the melt when a semicrystalline polymer is processed below its equilibrium thermodynamic melting temperature, T_m° ; the presence of vestigial crystals can lead to a higher nucleation density and reduced spherulite size. To investigate the possible influence of processing temperature on the morphology of the PEEK-based membranes, blend films were compression molded at two different melt temperatures, 380 and 400°C. The equilibrium melting temperature of PEEK has been reported in the range of 384 to 395°C,²⁸⁻³⁰ with minimal melting point depression upon blending with PEI.²¹ As such, the two experimental processing temperatures should correspond to conditions where few crystallites are present ($T_m = 400^\circ\text{C}$), or where a significant population of residual crystallites remains ($T_m = 380^\circ\text{C}$).

SEM micrographs of membrane cross-sections for extracted 25/75 PEEK/PEI blends melt crystallized under different conditions are shown in Figure 2. In addition to the two melt process temperatures used (380 and 400°C), two different isothermal crystallization temperatures were imposed: 260 and 300°C. Comparing Figure 2(a) to 2(b) ($T_c = 300^\circ\text{C}$), it is evident that melt process temperature has little influence on the morphol-

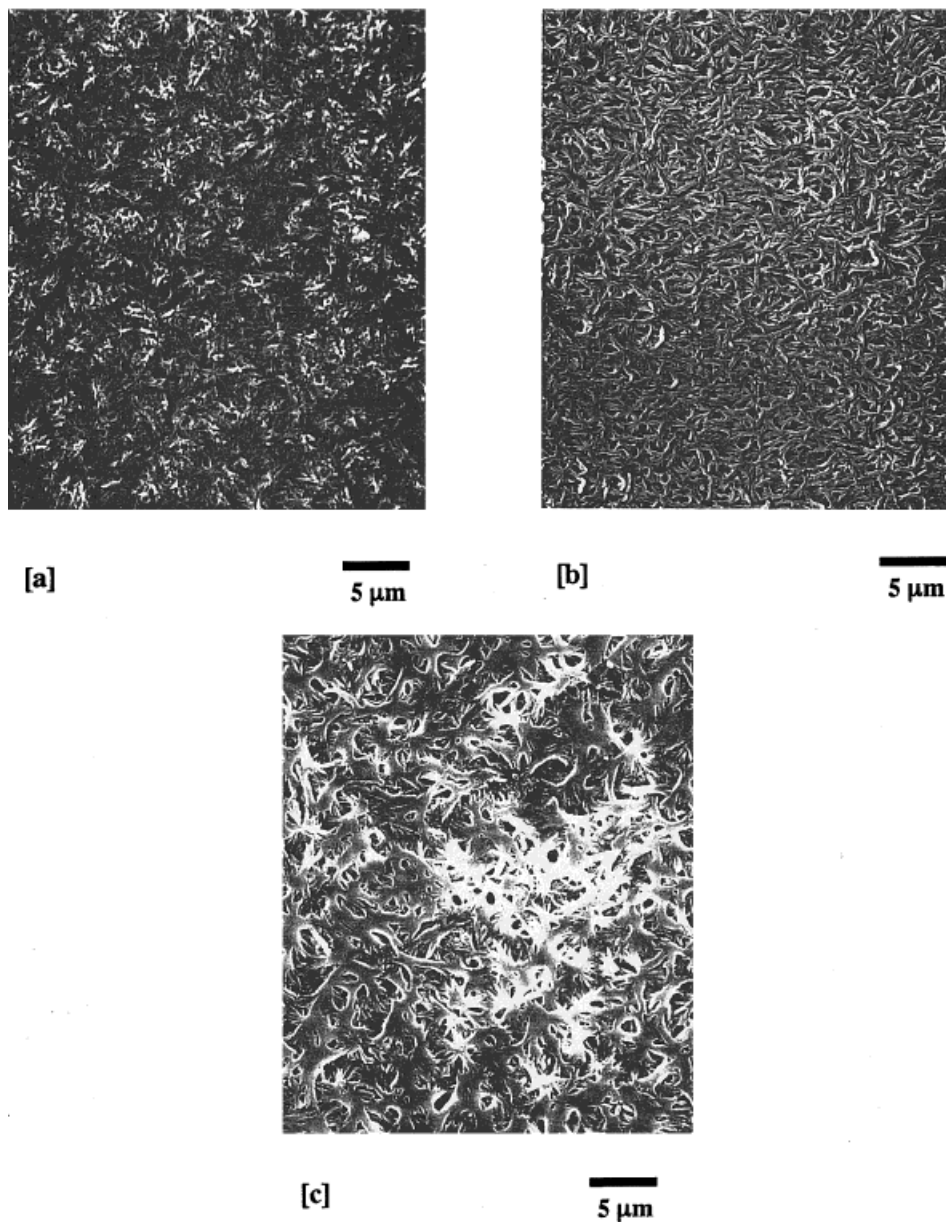


Figure 1 Scanning electron micrographs of membrane surface; initial blend composition of 25/75 PEEK/PEI. Samples cold crystallized at (a) 260°C; (b) 280°C; (c) 300°C. Magnification of 2000 \times .

ogy of the resulting membranes. Both cross-sections have relatively open structures with spherulites of similar size; the presence of large ($\sim 1 \mu\text{m}$) interspherulitic pockets reflects the low crystallization rate inherent to the 300°C annealing temperature. In Figure 2(c,d), the influence of melt process temperature is assessed for specimens melt crystallized at 260°C. Here again, the effect of melt process temperature appears minimal. The samples crystallized at 260°C display a very

fine pore structure that reflects PEI extraction from between fibrillar bundles.

These results are consistent with observations reported by Chiang and Lloyd for PPS membranes.¹⁴ They noted that for most conditions of dissolution temperature and polymer concentration, dense, highly nucleated morphologies were obtained; the domain size scale inherent to these morphologies was independent of prior dissolution temperature. When a high dissolution tem-

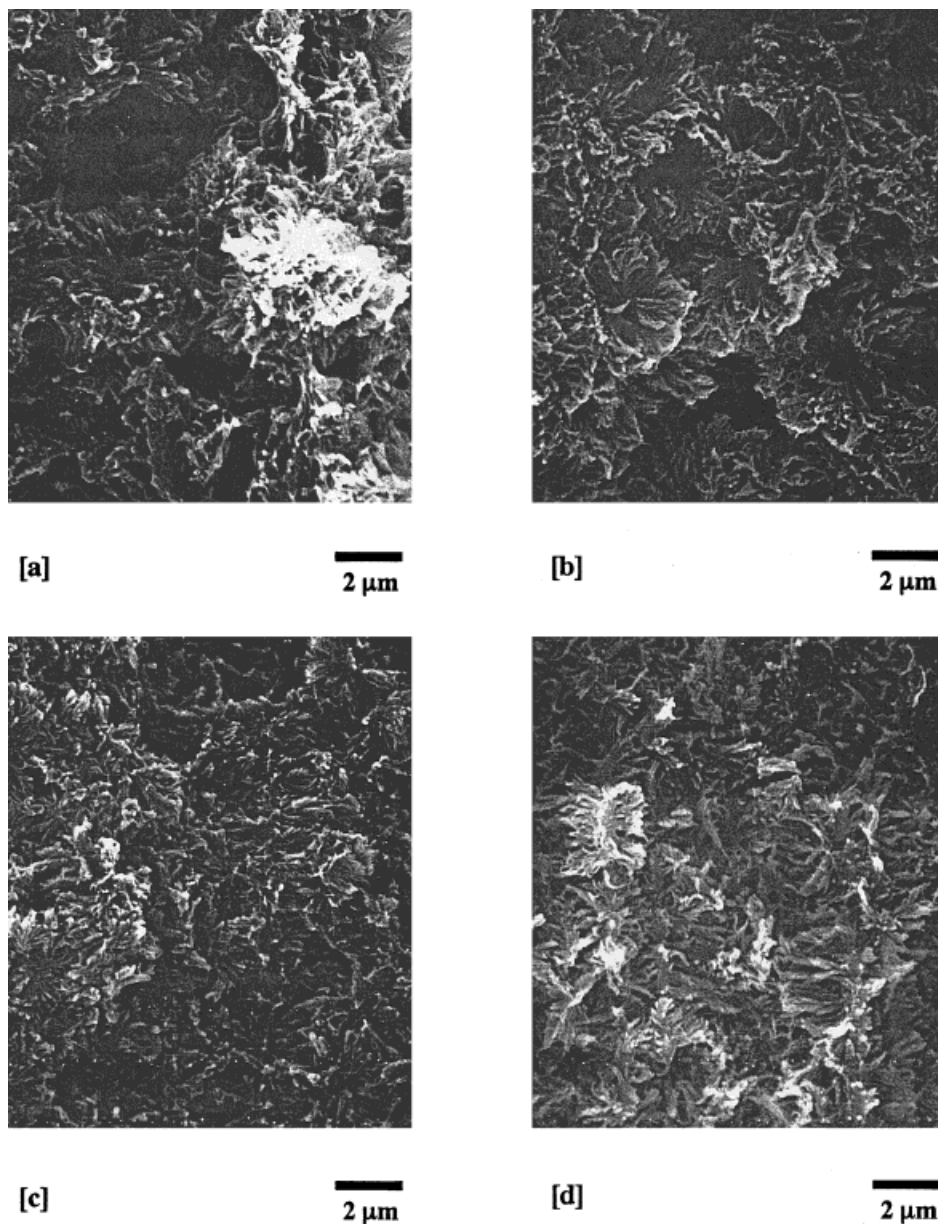


Figure 2 Scanning electron micrographs of membrane cross section; initial blend composition of 25/75 PEEK/PEI. (a) Sample prepared at 400°C, with crystallization at 300°C. (b) Sample prepared at 380°C, with crystallization at 300°C. (c) Sample prepared at 400°C, with crystallization at 260°C. (d) Sample prepared at 380°C, with crystallization at 260°C. Magnification of 5000 \times .

perature was imposed in combination with a relatively low overall polymer content, larger, more loosely packed spherulites were observed. The failure to observe this more open, well-developed spherulite structure in our PEEK membranes can be attributed to two factors. First, the imposed process temperature may not have been sufficiently high relative to T_m° to obtain a truly homo-

geneous melt, thus leading to a high “self-seeding” nucleation density in all cases. Second, the driving force for crystallization used when preparing the PEEK membranes, i.e., $\Delta T = T_m^\circ - T_c = 90$ to 130°C, was much higher than the value used in the PPS studies, $\Delta T = 60^\circ\text{C}$. A higher degree of undercooling leads to a higher nucleation density, and a correspondingly tighter structure. It should

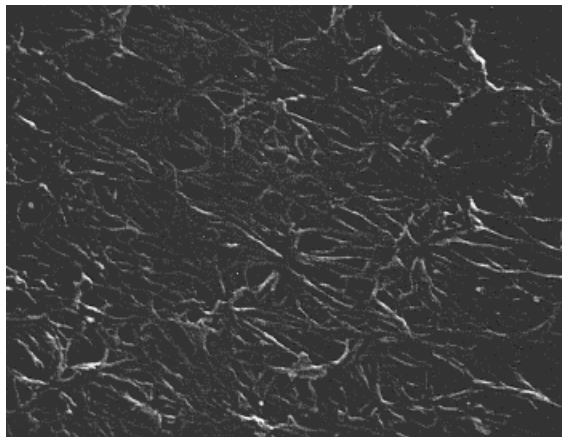


Figure 3 Scanning electron micrograph of membrane surface; initial blend composition of 25/75 PEEK/PEI. Sample cold crystallized at 300°C prior to diluent extraction. Uniaxial stretching at 305°C to 150% of original length. Magnification of 5000 \times .

be noted that the loose spherulite structure reported for the PPS membranes is undesirable, as these structures have weak connectivity and poor overall mechanical integrity.

For many applications, mechanical drawing of the extracted blend membranes is an essential "postprocessing" step for the achievement of useful properties. The PEEK/PEI blend membranes were successfully drawn at temperatures at or slightly above their isothermal crystallization temperatures. Figure 3 shows a representative photomicrograph of an extracted 25/75 PEEK/PEI blend sample that was stretched uniaxially in an environmentally controlled Instron testing machine at 305°C; the stretching rate was 0.25 mm min⁻¹, with a total extension of 150%. The membrane structure is highly fibrillated, with a network of drawn microfibrils radiating from the spherulite centers. The observed structure is quite similar to structures reported in the patent literature for stretched polyolefin membranes.^{3,4}

Mercury intrusion porosimetry was used to examine the pore characteristics of the PEEK/PEI membranes as a function of initial casting composition.^{31,32} Mercury intrusion porosimetry is an effective method for the examination of pore volume and surface area over a range of pore sizes from approximately 10 μm down to 0.005 μm (50 Å). The intrusion of mercury is governed by an inverse relationship between applied pressure and

pore radius. As such, caution is required at the high pressures involved (>500 bars; pore size less than ~ 0.015 microns), as these can lead to deformation and damage of the membrane structure.

Curves of intruded volume vs. pore radius for three PEEK/PEI blend membrane compositions are plotted in Figure 4; all samples were cold crystallized at 300°C prior to diluent extraction. Pore radius was calculated assuming cylindrical pores: the mercury surface tension was 0.48 N/m, and the contact angle with the polymeric surface was taken as 141.3°. A clear difference is evident in the pore volume distribution characteristics of each of the three compositions. The 75/25 PEEK/PEI membrane displays very little mercury intrusion, which is indicative of minimal porosity. The 25/75 and 50/50 PEEK/PEI membranes, however, show a significant degree of mercury intrusion, with the 25/75 membrane displaying a broader pore size distribution and a greater overall pore volume.

The volume distribution function, $D_v(r) = -dV/dr$, is plotted versus pore radius for the 25/75 and 50/50 PEEK/PEI membranes in Figure 5. Again, the 25/75 PEEK/PEI membrane shows a rather broad distribution of pore sizes, with considerable volume corresponding to pores in the range of 0.1 to 1 μm ; the volume distribution for the 25/75 membrane is centered at ~ 0.07 μm . The 50/50 PEEK/PEI membrane displays a

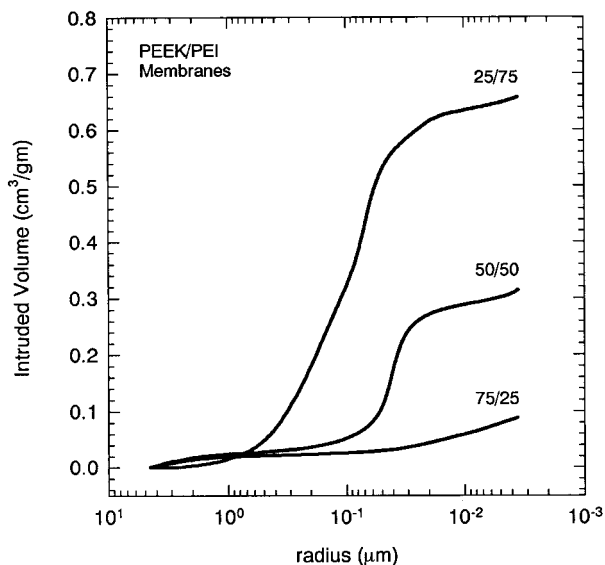


Figure 4 Mercury intrusion curves for PEEK/PEI membranes cold crystallized at 300°C prior to diluent extraction.

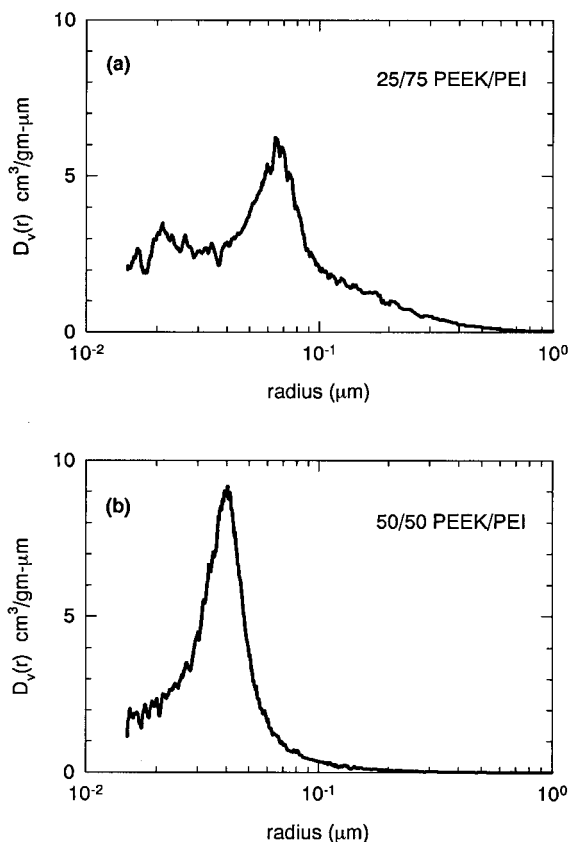


Figure 5 Volume distribution function $D_v(r)$ versus pore radius based on mercury intrusion porosimetry. (a) 25/75 PEEK/PEI initial composition; (b) 50/50 PEEK/PEI initial composition.

much narrower volume distribution, which is centered at $0.04 \mu\text{m}$. These results are consistent with the differences in morphology observed between the 25/75 and 50/50 PEEK/PEI membranes ($T_c = 300^\circ\text{C}$; see photomicrographs in ref. 23). Specifically, the 25/75 PEEK/PEI membrane displays micrometer-sized pockets which correspond to PEI extraction from interspherulitic regions. Thus, the distribution curve in Figure 5(a) reflects the presence of these relatively coarse pores, as well as finer interfibrillar pores. The morphology of the 50/50 PEEK/PEI membrane is dominated by interfibrillar pores, with very few interspherulitic pockets. This is consistent with the much narrower pore volume distribution evident in Figure 5(b).

The cumulative intruded volume and surface area of these membranes is reported in Table I for intrusion pressures up to 500 bars. Although the intruded volume for the 50/50 PEEK/PEI membrane is only about 45% of that measured

Table I PEEK/PEI Membrane Characteristics Determined via Mercury Intrusion Porosimetry; Cumulative Values Based on Intrusion Pressures up to 500 Bars

Initial Composition	Intruded Volume (cm^3/g)	Surface Area (m^2/g)
PEEK/PEI		
25/75	0.63	15.7
50/50	0.28	12.4

for the 25/75 membrane, the cumulative surface areas are comparable. This result suggests the presence of a large number of smaller pores in the 50/50 PEEK/PEI membrane, which is consistent with the intrusion curves presented above.

It should be noted that the pore size distribution obtained for the 50/50 PEEK/PEI membrane is similar to results originally reported in the patent literature for extracted blends based on 55% PEEK, 45% PEI. Dubrow and Froix³⁴ reported an average pore size of $0.03 \mu\text{m}$ for this composition, with no pores greater than $0.07 \mu\text{m}$.

Pure water flux measurements were carried out on as-cast and drawn PEEK/PEI flat sheet membranes in an effort to compare the permeability of these materials with values reported in the patent literature for PEEK hollow fibers. Water flux as a function of initial membrane composition is reported per unit applied pressure in Table II; the thickness of the membranes was approximately $100 \mu\text{m}$. A systematic decrease in flux is observed with decreasing diluent content in the initial blend; the 75/25 membrane composition shows no water flux at the applied pressure of 3.8 bars, which is consistent with the mercury intrusion studies presented above. The value ob-

Table II Pure Water Permeability Characteristics for PEEK/PEI Membranes Cold Crystallized at 300°C Prior to Diluent Extraction

Initial Composition PEEK/PEI	Water Permeability $\text{L h}^{-1} \text{m}^{-2} \text{bar}^{-1}$
25/75	79
35/65	45
50/50	36
75/25	0

Measurements conducted at 25°C , 3.8 bars applied pressure.

Table III Pure Water Permeability Characteristics for 25/75 PEEK/PEI Membranes as a Function of Cold Crystallization Temperature

Crystallization Temperature (°C)	Water Permeability L h ⁻¹ m ⁻² bar ⁻¹
300	79
280	11
260	3

Measurements conducted at 25°C, 3.8 bars applied pressure.

tained for the 25/75 PEEK/PEI membrane, 79 L h⁻¹ m⁻² bar⁻¹, is comparable to values reported for hollow fiber membranes based on an initial PEEK content of 27 to 30%. Specifically, Damrow et al. reported hollow fiber flux values ranging from approximately 100 to 350 L h⁻¹ m⁻² bar⁻¹ for the PEEK-based membranes;¹⁶ the hollow fiber wall thickness for these membranes ranged from 65 to 90 μm.

Flux results for the 25/75 PEEK/PEI membranes are presented as a function of cold-crystallization temperature in Table III. A sharp decrease in water flux is observed with decreasing crystallization temperature, which reflects a shift from a largely interspherulitic pore morphology to a morphology dominated by fine, interfibrillar pores (see Fig. 1). Uniaxial stretching of 25/75 PEEK/PEI membranes cold crystallized at 300°C resulted in a dramatic increase in water permeability: the measured permeability for the 150% stretched sample depicted in Figure 3 was 4090 L h⁻¹ m⁻² bar⁻¹ (applied pressure of 1.4 bars), which corresponds to a 50-fold increase compared to the as-cast 25/75 PEEK/PEI membrane.

CONCLUSIONS

The morphology and bulk characteristics of a series of membranes prepared from PEEK/PEI blends have been examined using scanning electron microscopy, mercury intrusion porosimetry, and water flux measurements. The membrane structure was sensitive to both initial blend composition and crystallization temperature, with the resulting morphology reflecting the kinetics of phase separation. Membranes prepared with lower initial diluent content (e.g., 50/50 PEEK/PEI) or at lower crystallization temperatures dis-

played a relatively narrow distribution of fine, interfibrillar pores. Membranes prepared with higher diluent content (e.g., 25/75 PEEK/PEI) or at higher crystallization temperatures displayed a broad pore distribution, with the coexistence of coarse interspherulitic pores and interfibrillar pores. Postprocess drawing of the as-cast membranes led to a fibrillated network structure with markedly higher water flux characteristics.

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