Hollow Fiber Microfiltration Membranes from Poly(ether ether ketone) (PEEK)

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ABSTRACT: A procedure for obtaining high performance large internal diameter (ID; >1 mm) hollow fiber microfiltration membranes from poly(ether ether ketone) (PEEK) is presented. A simple mixture of isomers of diphenylphthalate is a good solvent for employing the thermal-phase inversion process to obtain PEEK membranes. Obtaining large ID hollow fibers with substantial transmembrane flux requires sufficient melt strength during spinning to prevent excessive draw of the extruding fiber. The use of a second leachable polymer to the blend satisfies the conditions, and polysulphone (PS) is found to provide superior membranes relative to either poly(etherimide) (PEI) or poly(ether sulphone) (PES) as a second polymer. PEEK membranes obtained by this process yield better chemical resistance to a concentrated warm surfactant/oil solution. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 175–181, 1999

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

INTRODUCTION

Cross-flow microfiltration for concentration of suspended particles in solution is widely practiced for a variety of applications.^{1–3} As the techniques of cross-flow filtration become more widely known, their application spreads to more demanding solution streams. A wide variety of polymeric materials are commonly used for making membranes.⁴ Many of these materials are easily processed into membranes using the thermally induced phase inversion process (TIP).⁵ TIP 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.⁶⁻⁸ 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.

Current polymer membrane materials are practical for low-temperature aqueous separations. More demanding separations generally require the use of ceramic membranes, although these are far more expensive and more difficult to make than polymeric membranes.² The new class of semicrystalline materials such as poly(ether ether ketone) (PEEK)⁹ and poly(phenylene sulfide) (PPS)^{10,11} 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. This paper describes methods for preparing highperformance microfiltration membranes from PEEK.^{12,13} Particularly, these membranes were prepared for their application in large internal diameter (ID) hollow fiber (tubule) form, a mode that results in the highest cross-flow efficiency. Preparation of ultrafiltration film membranes will be covered in a subsequent publication.

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EXPERIMENTAL

PEEK 450G was obtained from Victrex Corporation (West Deptford, NJ) under the trade name Victrex. Polysulphone (PS) was obtained from Amoco Plastics (Alpharetta, GA) under the tradename Udel. Poly(etherimide) PEI was obtained from GE Plastics (Pittsfield, MA) under the tradename Ultem 1000. A blend of 75% diphenylisophthalate (DPIP)/25% diphenylterephthalate (DPTP) was obtained from Hoechst Celanese (Charlotte, NC). DPTP and DPIP were purchased separately from Sloss Industries (Birmingham, AL). All materials were used as received.

Polymer solutions were obtained by first blending the DPIP/DPTP with the PS, poly(ether sulphone) (PES), or PEI 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 heated to 340°C to assure uniform blending. The resin kettle temperature was controlled carefully using an Oron (Schaumburg, IL) temperature controlled 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 PEEK is fully mixed into the solution, the blend is dark brown and transparent (when observed through a small path length). The blend is then carefully poured from the kettle into a metal pan, covered, and allowed to cool quiescently. The light brown PEEK/polymer/DPIP/DPTP blend was then chipped in an IMS Co. (Chagrin Falls, OH) grinder to a size suitable for feeding to an extruder.

Large ID hollow fibers were extruded on a Killion (Cedar Grove, NJ) $\frac{3}{4}$ single screw extruder with a general purpose screw with a length/diameter (L/D) ratio of 24. The molten polymer solution was fed to a Zenith Industries (Patterson, SC) melt pump and subsequently to a spinnerette designed specifically for extrusion of high-viscosity molten polymer into a tubule form. Hollow fibers were spun employing a nitrogen core gas to maintain the ID upon exiting the spinnerette. A face heater was employed to prevent phase separation occurring at the spinnerette face. Extruder temperatures ramped from 260°C at the feed throat to 330°C in the melt zone and melt pump, and then declined to approximately 310°C at the spinnerette face. Extruder screw speed was controlled to maintain a constant suction pressure of 300 psi. Melt zone and pump temperatures could



Figure 1 Fiber testing configuration. Polycarbonate cell is filled with water during test and usually inverted. Water is collected underneath and then weighed. Flux is then normalized to transmembrane pressure, membrane surface area, and collection time.

be increased gradually during fiber spinning to maintain discharge pressures below 2500 psi.

The large ID hollow fibers were drawn at a constant rate using a homemade godet and subsequently wound on a core using a tension-controlled Leesona winding instrument. Spinneretteto-godet gap distances were between 6 and 12 in. Godet speeds were run between 8 and 20 linear ft/ min. Membrane was leached in methylene chloride or 1-methyl-2-pyrrolidinone (NMP) until the weight of the fibers no longer decreased due to removal of the PS, PES, or PEI and DPIP/DPTP. Mass balance typically showed that at least 98% of the solvent and sulfone-containing polymer could be recovered through the leaching process. The missing mass is believed to be a result of evaporating solvent during the extrusion process. Hollow fibers from blends containing PEI typically could not be fully leached as PEI continued to be extracted after numerous extractions, leaving the fiber as much as 10% heavier than could be accounted for by its PEEK content. Fibers were not leached under constant tension and fiber shrinkage during this step was not controlled. PEEK hollow fiber sizes were a function of various process parameters such as melt pump and godet speed and spinnerette geometry. Fiber diameter variability usually varied <10% but could assume an oblong shape if the Leesona tension adjustment was too high, which would cause compression to the wound fibers. Membrane pure water flux was measured by insertion of several fibers into a Dow cell (see Fig. 1). Prior to water



Figure 2 Ternary composition diagram representing weight percentages of blends containing PEEK, PS, and DPIP/DPTP for making microfiltration membranes. Cross hatched area represents weight percentages where blends were prepared.

flux measurement, the fibers were wet with ethanol. The ethanol in the fibers was then displaced by thorough replacement with high-performance liquid chromatography (HPLC) grade water. Fibers were pressurized from the outside and the flux of water pushed through the membrane walls was collected from the membrane openings potted in epoxy. Following a definite time interval, the water weight was measured and the flux normalized to membrane surface area, transmembrane pressure, and collection time. Maximum and mean pore size were determined by bubble point using ethanol according to ASTM F 316.25 SEM were obtained by Rosemary Ross of the Dow Analytical Department using a methanol soak followed by a freeze fracture.

RESULTS AND DISCUSSION

The very features that make PEEK an attractive candidate for a high-performance membrane material make it a difficult material to process. The solvent resistance of PEEK requires that relatively exotic solvents be employed to obtain solution.¹⁴ DPTP and DPIP are both very good solvents for PEEK with boiling points about 410°C (well below the extrusion temperature). DPIP used alone as a solvent has a narrower window of temperature-independent concentrations with PEEK than does DPTP. When blends of DPTP/PS

and PEEK are extruded, the resulting membrane has very good properties but is difficult to handle due to the highly brittle crystalline nature of the blend at room temperature. The incorporation of DPIP into the blend delays recrystallization of the solvent system for about 48 h, allowing easy handling of the fiber. This delayed recrystallization feature of the mixed solvent system is presumably due to their acting as a highly soluble impurity delaying each other's recrystallization. The solvent/PEEK blend exhibited concentration-independent recrystallization temperatures of the PEEK-rich phase between 40 and 24 wt % PEEK concentration. This observation suggests the presence of liquid/liquid phase separation mechanism prior to solidification at that concentration range.^{15,16} Although a liquid/solid phase separa-



Figure 3 Scanning electron micrographs of PEEK microfiltration membranes from a ternary blend containing 30% PEEK/20% PES/50% diphenylphthalate isomers.



Figure 4 Scanning electron micrographs of PEEK microfiltration membranes from a ternary blend containing 30% PEEK/20% PS/50% diphenylphthalate isomers.

tion mechanism can produce efficient membranes, the best membrane properties (the combination of narrow pore size distribution and high flux) are usually obtained from a liquid/liquid separation mechanism.⁵

To obtain a large ID hollow fiber, the extruding polymer blend must have sufficient viscosity so it does not rapidly draw down prior to solidification upon exiting the spinnerette. To obtain the necessary viscosity with a binary blend of PEEK and diphenylphthalates, approximately 70 wt % PEEK is required. The resulting hollow fiber, although porous, had no transmembrane flux. An alternative approach is to add a second polymer to the PEEK/diphenylphthalate blend. Such a second polymer must be miscible with PEEK in the range of phase-spinning temperatures but insoluble at room temperature to obtain a narrow



Figure 5 Scanning electron micrograph of PEEK microfiltration membrane from a ternary blend containing 30% PEEK/20% PEI/50% diphenylphthalate isomers.

pore-size distribution in the microfiltration range. The polymer must also be soluble in the leaching solvent. The effect of the second polymer on phase-separation kinetics is also a factor in obtaining an optimized membrane.

Three polymers met the initial conditions exhibiting solubility with PEEK at elevated temperatures, insolubility at lower temperatures, and leachability using available solvents. These polymers were PS, PES,^{17–19} and PEI.^{20,21} It was previously reported,²² and was our experience, that PEI is too miscible with PEEK and results in a



Figure 6 Relationship between ethanol bubble point and PS content in 34% PEEK blends with diphenylphthalate ester isomers. Maximum pore size is obtained by dividing 9.25 by the measured bubble point (units in micrometers).



Figure 7 Porosity versus gravimetrically determined PEEK content of cast PEEK film membranes.

blend from which all the PEI cannot be removed. PES, on the other hand, exhibits a relatively rapid phase separation from the molten polymer blend.¹⁸ PEEK membranes from its ternary blend with DPIP/DPTP and PES were functional but exhibited a highly coarsened structure with relatively large maximum and mean pore sizes for a given concentration. PS, especially the low molecular weight commercial variety (Grade 3703), exhibits a moderation between the two extremes. Figure 2 is a ternary composition diagram of the blend compositions explored in this study. Figures 3-5 are SEM micrographs of gross and micromorphology of tubules obtained from PEEK/ PES/DPIP/DPTP and PEEK/PS/DPIP/DPTP blends and PEEK/PEI/DPIP/DPTP blends.

For a given PEEK content, the maximum pore size of a membrane as determined from ethanol bubble point varies linearly with the weight amount of PS in the blend varying from approximately 0.12 μ m at 16% PS to approximately 0.3 μ m at 25% PS (Fig. 6). Mean pore sizes were



Figure 8 Relationship between PEEK content and water flux. Lines through points indicate the range of fluxes observed for different diphenylphthalate/PS ratios.



Figure 9 Performance of Dow experimental microfiltration membranes from (A) PEEK and (B) commercial microfiltration membranes from PES. Initial time values are arbitrary. Effluent stream is a proprietary mixture of anionic and nonionic surfactants at 5% concentrations in water and 1% commercial corn oil. Units of permeate flux (gfd/psi) is gallons of permeate flux/(ft² membrane surface area × day × psi transmembrane pressure).

generally 50% of the maximum pore size measured by bubble point. Porosity of the membranes was determined from cast membrane films of the polymer blends to facilitate measurement of volume. The porosity was then determined from eq. (1).

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

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 differential scanning calorimetry (DSC) data] and the known²³ densities of amorphous and crystalline PEEK (amorphous = 1.2626 g cc⁻¹ crystalline = 1.4006 g cc⁻¹) and by using a theoretical heat of fusion of 100% crystalline PEEK of 130 J g^{-1.24} Figure 7 shows the relationship between membrane porosity and PEEK content in the polymer blend used for making the membrane. The relationship is approximately a straight

line with the porosity being about 5% less than predicted just from gravimetric considerations. The deficit is presumably due to membrane shrinkage during the leach step.

The most important influence on pure water transmembrane flux for PEEK/PS/DPIP/DPTP membranes was the PEEK concentration. Figure 8 shows the effect of PEEK concentration on pure water flux. The membrane fluxes measured are from ternary blends, thus each PEEK concentration can vary the weight fraction of PS independently. The lines through the points provide the range of water flux values measured over the range of permutations tried. The relationship is once again approximately linear.

PEEK tubule membranes were fabricated into a module for the purpose of comparison to the performance of a commercial PES membrane in a similar configuration. The stream was chosen as a demonstration of the membrane's ability to withstand harsh solvents under elevated temperatures. The stream chosen was a Dow Chemical (Midland, MI) proprietary blend of nonionic and anionic surfactants denoted XU11301, a product intended for semiagueous metal cleaning operations with the addition of 1% commercial food grade corn oil. Figure 9 shows the flux behavior of 1 ft² membrane modules resulting from exposure to the surfactant/oil stream with temperature and time. The data shows that the PEEK membrane is unaffected by the stream and the flux increases slightly with temperature due to the decreasing viscosity of the surfactant-laden stream. In contrast, the PES membrane shows an extended decrease in flux with time and temperature. This effect is presumably due to swelling of the PES membrane by the components in the stream.

CONCLUSIONS

High-performance tubule membranes from the high-performance polymer PEEK were prepared from a ternary blend including PS, DPIP, and DPTP. PS provides sufficient melt strength to the extruding blend to minimize the fiber draw and also moves the pore-size distribution to larger values. The diphenylphthalate esters are a very useful solvent system for PEEK for making membranes, and when used in mixtures, make the extruded membrane more flexible prior to leach by slowing the recrystallization rate. We showed that PEEK membranes provide superior performance to a polysulphone membrane in exposure to a warm surfactant/oil stream.

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