

Sulfonated Poly(ether ether ketone)-Induced Porous Poly(ether sulfone) Blend Membranes for the Separation of Proteins and Metal Ions

G. Arthanareeswaran,¹ P. Thanikaivelan,² M. Raajenthiren³

¹Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli 620015, India

²Centre for Leather Apparel and Accessories Development, Central Leather Research Institute, Council of Scientific and Industrial Research, Adyar, Chennai 600020, India

³Department of Chemical Engineering, Anna University, Chennai 600025, India

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ABSTRACT: Asymmetric ultrafiltration (UF) membranes were prepared by the blending of poly(ether sulfone) (PES) and sulfonated poly(ether ether ketone) (SPEEK) polymers with *N,N'*-dimethylformamide solvent by the phase-inversion method. SPEEK was selected as the hydrophilic polymer in a blend with different composition of PES and SPEEK. The solution-cast PES/SPEEK blend membranes were homogeneous for all of the studied compositions from 100/0 to 60/40 wt % in a total of 17.5 wt % polymer and 82.5 wt % solvent. The presence of SPEEK beyond 40 wt % in the casting solution did not form membranes. The prepared membranes were characterized for their UF performances, such as pure water flux, water content, porosity, and membrane hydraulic resistance, and morphology and melting tempera-

ture. We estimated that the pure water flux of the PES/SPEEK blend membranes increased from 17.3 to 85.6 L m⁻² h⁻¹ when the concentration of SPEEK increased from 0 to 40 wt % in the casting solution. The membranes were also characterized their separation performance with proteins and metal-ion solutions. The results indicate significant improvement in the performance characteristics of the blend membranes with the addition of SPEEK. In particular, the rejection of proteins and metal ions was marginally decreased, whereas the permeate flux was radically improved. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 995–1004, 2010

Key words: blending; hydrophilic polymers; membranes; morphology; poly(ether sulfones)

INTRODUCTION

In recent years, ultrafiltration (UF) membranes have been used for a wide range of applications, such as the concentration or purification of solutes, wastewater treatment, and solute separation. However, the major problem in the extensive use of membranes is membrane fouling, which results in reduced rate and flux during the operation.¹ It has generally been known that increasing the hydrophilicity can improve the antifouling properties of membranes. Many studies on the hydrophilization of hydrophobic UF membrane materials have been carried out.^{2–4} Many studies have been conducted concerning the addition of hydrophilic polymers such as poly(ethylene glycol) or poly(vinyl pyrrolidone) in the membrane casting solution to improve

the membrane performance.^{5,6} In addition, surface modifications of the hydrophobic membrane materials by sulfonation, amination, and carboxylation have been widely studied.^{7–9} Charged polymers not only increase the hydrophilicity of membranes but also provide an increased product rate of feed solution. In previous studies,^{10,11} sulfonated poly(ether ether ketone) (SPEEK) was introduced to modify cellulose acetate membranes to improve the performance of UF. SPEEK was blended with cellulose acetate in *N,N'*-dimethylformamide (DMF) as solvent over a compatible range.

Poly(ether sulfone) (PES) has been widely used as a membrane material because of its excellent chemical resistance, good thermal stability, and mechanical properties.¹² It can be imagined that PES has a crystalline structure to some degree because of the harder benzene ring and softer ether bond existing in the structure. It has become an important separation membrane material; however, its hydrophobicity, controlled by the PES structure, leads to low flux and quick fouling, which greatly affect the application fields and the life of the membrane. Hence, it is necessary to modify the PES membrane surface by physicochemical methods and improve its hydrophilicity. To increase the hydrophilicity of the PES

Correspondence to: G. Arthanareeswaran (arthanaree10@yahoo.com).

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membrane, poly(vinyl pyrrolidone) is often blended into PES.¹³

SPEEK is a good hydrophilic polymer that is widely used in the preparation of phase-inversion membranes. SPEEK has a wide range of miscibility with PES, poly(vinylidene fluoride), polyacrylonitrile, poly(vinyl chloride), cellulose triacetate, and so on.¹⁴ In recent years, the blending of SPEEK with base polymers, such as polysulfone, poly(ether imide), and poly(vinylidene fluoride), has been thoroughly studied for membrane formation for fuel cell applications.^{15–18} In recent studies, PES/SPEEK blend membranes were reported by Wu et al.¹⁹ They prepared PES/SPEEK blend membranes in *N*-methyl-2-pyrrolidinone as a solvent by solution casting. They investigated the water uptake, methanol uptake, permeability, and proton conductivity of the PES/SPEEK blend membranes. During the preparation of the membranes, the solvent and polymer compositions were influenced the performance of the membranes. However, studies on SPEEK as a blend polymer with PES on membrane formation for UF applications such as metal-ion and proteins separation have been very limited.²⁰

In this investigation, we attempted to prepare membranes in all compatible compositions of PES/SPEEK in DMF as a solvent for UF application. The synthesized membranes were characterized for pure water flux, membrane hydraulic resistance, and water content. The cross-sectional morphologies of the prepared membranes were also studied with scanning electron microscopy (SEM). Furthermore, the effect of the concentration of SPEEK in the casting solution on the rejection and permeate flux of proteins, such as bovine serum albumin (BSA), egg albumin (EA), pepsin, and trypsin, and toxic heavy metal ions, such as Cu(II), Co(II), Zn(II), and Cd(II), were also investigated.

EXPERIMENTAL

Materials

Commercial-grade PES (Gafone 3300) was obtained as a gift sample from Gharda Chemicals Pvt., Ltd.

(India) and was used as supplied. SPEEK was kindly supplied by PCI Membranes (Basingstoke, UK); this material had an ion-exchange capacity of 2.1 mequiv/g. DMF and sodium lauryl sulfate were obtained from Qualigens Fine Chemicals, Glaxo India, Ltd. (India); these materials were analytical grade. DMF was sieved through 4-Å molecular sieves to remove moisture and stored under dry conditions before use. Disodium hydrogen orthophosphate anhydrous and monosodium dihydrogen orthophosphate heptahydrate were procured from CDH Chemicals, Ltd. (India). Proteins, namely, BSA [weight-average molecular weight (M_w) = 69 kDa], pepsin (M_w = 35 kDa), and trypsin (M_w = 20 kDa) were purchased from SRL Pvt., Ltd. (India). EA (M_w = 45 kDa) was obtained from the Council of Scientific and Industrial Research, Bio-Chemical Center (New Delhi, India). Poly(ethylene imine) (PEI) was procured from Fluka (Germany). Analytical-grade copper sulfate, cobalt sulfate, zinc sulfate, and cadmium sulfate were procured from Merck (India) and were used as received. Deionized and distilled water was used for the preparation of protein and metal-ion solutions.

Preparation and characterization of the blend membranes for UF applications

The two polymers were dissolved in DMF (17.5 wt % of the total polymer concentration) and kept under constant mechanical stirring in a two-necked, round-bottom flask for 3 h at 40–45°C. A series of such polymer solutions were prepared by variation of the composition of PES and SPEEK with increments of 10 wt % SPEEK, as shown in Table I. The homogeneous polymer solutions were allowed to stand for 1 h to eliminate air bubbles before they were cast. The dope solution was poured and spread onto a glass plate with a doctor blade. The thickness of the membranes was adjusted to 0.20 ± 0.02 mm. Before casting, a gelation bath of 2 L, consisting of 2.5% (v/v) DMF and 0.2 wt % sodium lauryl sulfate in distilled water (nonsolvent), was prepared and ice-cooled to $12 \pm 2^\circ\text{C}$. The casting and gelation conditions of prepared membranes are shown in

TABLE I
Characterization of the PES/SPEEK Blend Membranes

Polymer composition (17.5 wt %)		DMF (wt %)	Pure water flux (L/m ² h)	Water content (%)	Porosity (%)	Hydraulic resistance of the membrane (kPa/L m ⁻² h ⁻¹)
PES (%)	SPEEK (%)					
100	0	82.5	17	70	59	13.6
90	10	82.5	31	78	64	9.3
80	20	82.5	44	82	70	7.2
70	30	82.5	50	86	78	4.1
60	40	82.5	86	89	93	2.7

TABLE II
Film-Casting and Gelation Conditions for the
PES/SPEEK Blend Membranes

Condition	Value
Temperature of the casting solution (°C)	24–26
Temperature of the casting atmosphere (°C)	20–23
Humidity of the casting atmosphere (%)	60–65
Solvent evaporation (min)	30
Temperature of the gelation bath (°C)	10–14
Period of gelation (h)	>12
Thickness of the membrane (mm)	0.18–0.22

Table II. After 30 min of solvent evaporation in the casting chamber, the glass plate, along with the polymer film, was immersed in the gelation bath. The membranes were kept in the gelation bath overnight and then washed with deionized water before the UF experiments. Similar casting and gelation conditions were used for all of the membranes.

UF experimental setup

The membranes were cut into circular disks with a diameter of 76 mm for setup in a stirred UF cell (UF cell-XFUFO7601-model, Millipore (I), Ltd., Bangalore) fitted with a Teflon-coated magnetic paddle. The UF experiments were carried out in a 400-mL feed solution and with effective membrane area available of 38.5 cm². The solution filled in the cell was stirred at 400 rpm with a magnetic stirrer. All of the experiments were carried out at 30 ± 2°C and with a 345-kPa transmembrane pressure. The schematic diagram of the stirred UF cell is shown in Figure 1. All membranes were prepared three times under the same conditions. The value of flux or rejection of each membrane composition was taken as an average from three membranes.

Pure water flux

Membranes were placed in a static UF evaluation cell with an active area of 38.5 cm² and compressed with pure water at a constant stirring speed of 400 rpm for 10 min at 345 kPa. The pure water flux was calculated by measurement of the volume of permeates that penetrated the membrane per unit time.

Water content

Membrane samples were cut to the desired size and soaked in water for 24 h and weighed immediately after the free surface water was blotted. These wet membranes were dried for 12 h at 100 ± 2°C and weighed. From the dry and wet weights of the samples, the percentage water contents were calculated with an equation given elsewhere.¹⁰

Porosity

After the membranes were equilibrated in water as described previously, the volume occupied by water and the volume of the membrane in the wet state were determined according to the procedure reported by Chen et al.²¹ The porosity of the membranes was determined with eq. (1):

$$\text{Porosity} = \frac{(W_1 - W_2)}{\rho_{\text{water}} V_T} \times 100 \quad (1)$$

where ρ_{water} is the density of pure water at 25°C (kg/m³), V_T is the apparent volume of the membrane in the wet state (m³), and W_1 and W_2 are the weights of the membranes in the wet and dry states, respectively. V_T was calculated with the following equation:

$$V_T = \frac{(W_1 - W_2)}{\rho_{\text{water}}} + \frac{W_2}{D_p} \quad (2)$$

where D_p is the density of the dry-state membrane (kg/m³).

Membrane hydraulic resistance

To determine the membrane hydraulic resistance, the pure water flux of the membranes was measured at different transmembrane pressures, namely, 69, 138, 207, 276, and 345 kPa. The variation of pure water flux was plotted as a function of transmembrane pressure for all of the prepared membranes. The hydraulic resistances of the membranes were determined from the inverse of slopes with the following equation:

$$R_m = \frac{\Delta P}{J_w} \quad (3)$$

where ΔP is the transmembrane pressure, J_w is the pure water flux, and R_m is the hydraulic resistance of the membrane.

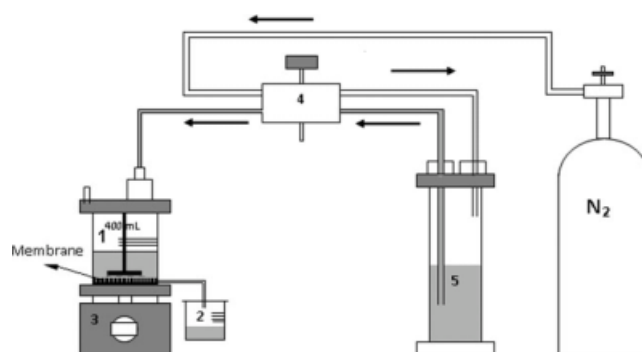


Figure 1 Schematic diagram of stirred ultrafiltration kit cell: (1) Stirred UF cell, (2) permeate, (3) magnetic stirrer, (4) selector, and (5) reservoir.

Morphological studies

The membranes were cut into small pieces and mopped with filter paper. These pieces were immersed in liquid nitrogen for 20–30 s and frozen. The frozen bits of membranes were broken and kept in a desiccator. These membrane samples were used for SEM studies. The membrane samples were mounted on studs and gold-sputtered.⁶ The cross sections of the membranes were viewed with a JEOL JSM-840A scanning electron microscope (Beggroke, England).

Differential scanning calorimetry (DSC) analysis

The developed PES/SPEEK blend and pure PES membrane samples were tested with a differential scanning calorimeter (model Q20, Universal V4.0C TA Instruments, USA). The samples were heated up to 160°C in a nitrogen atmosphere at a rate of 10°C/min. The nitrogen flow was maintained at a level of 50 mL/min.

Separation studies

Protein removal

Aqueous solutions of BSA, EA, pepsin, and trypsin were prepared at a concentration of 1000 ppm by the dissolution of the proteins (0.1 wt %) individually in phosphate buffer (0.5M, pH 7.2). As the separation of a high-molecular-weight protein may hinder the separation of low-molecular-weight protein, the separation was first done for the low-molecular-weight protein then progressively for high-molecular-weight protein. Hence, the separation was performed in the order: trypsin, pepsin, EA, and BSA.

The stirred UF cell was filled with protein solution and maintained at a constant pressure of 345 kPa. After UF, the permeate solutions of the corresponding membranes were collected in graduated tubes and analyzed for the concentration of protein with an ultraviolet–visible spectrophotometer (model UV-160A, Shimadzu, USA) at the maximum wavelength of 280 nm. The protein rejection percentage was calculated from the concentrations of protein in the feed (C_f) and permeate (C_p) with the following equation:

$$\text{Protein rejection(\%)} = [1 - (C_p/C_f)] \times 100 \quad (4)$$

Upon completion of every run, the UF cell was emptied, and the membrane was removed and washed gently with pure water to remove of the adhered protein and then replaced in the cleaned cell.

Metal-ion removal

PEI was used to complex the metal ions for their separation through the developed UF membranes.²² To determine the influence of PEI on the metal-ion rejection, preliminary experiments were carried out to separate the metal salt solutions in the absence of PEI with the pure PES membrane after the pH was adjusted to 6 ± 0.25 . Virtually all of the metal ions permeated through the membrane. Hence, PEI was used to complex the metal ions. Solutions of Cu(II), Co(II), Zn(II), and Cd(II) were prepared at a concentration of 1000 ppm in a 1 wt % aqueous solution of PEI. The pH of these solutions was adjusted to 6 ± 0.25 by the addition of a small amount of either 0.1M HCl or 0.1M NaOH. The solutions were then thoroughly mixed and allowed to stand for a day for the completion of binding.⁶ Metal-ion removal was carried out as mentioned previously through the UF cell, and the permeate solutions of the corresponding membranes were collected in graduated tubes. They were analyzed for the concentration of the metal ions with an atomic absorption spectrometer (PerkinElmer 3110, Yokohama, Japan). The percentage rejection of the metal ions were calculated from the concentration of metal ions in feed and permeate with eq. (4).

RESULTS AND DISCUSSION

Membrane preparation

Blend UF membranes based on PES and SPEEK with various compositions were prepared. The miscibility of the selected polymers was confirmed by the homogeneity of the casting solution and uniformity of the resulting membranes. The maximum possible blend composition was found to be 60/40 wt % PES/SPEEK, beyond which phase separation occurred and the membrane did not form. Particularly when the composition of PES/SPEEK was 50/50 wt %, the casting solution became turbid at room temperature; this indicated a lower miscibility of SPEEK with PES at the 50/50 wt % composition. When a membrane is formed by phase inversion, a porous top layer is formed because of phase separation caused by diffusional nonsolvent transport into the polymer solution.^{23,24} Thus, it is reasonable to relate the number of pores to the number of microscopic locations where such separation occurs. The interphase regions between SPEEK and PES were probably the locations at which phase separation was most likely. In addition, as SPEEK is a highly hydrophilic polymer, the presence of SPEEK will favor water ingress, which will increase phase separation. Hence, with a higher weight percentage of SPEEK, when the membrane was cast and

immersed in a gelation bath, two separate layers were formed because of complete phase separation. This showed the incompatibility between the two polymer components at higher (50/50 wt %) concentration ratios. Thus, membranes with compositions of 100/0, 90/10, 80/20, 70/30, and 60/40 wt % PES/SPEEK were prepared for further study.

Characterization of the blend membranes

Pure water permeability (PWP)

PWP is the key specification of any type membrane and must be determined essentially. PWP of all of the membranes was measured to evaluate their water permeability and reproducibility. All of the membranes were subjected to pure water flux at a pressure of 345 kPa under steady-state conditions and at a constant sampling period. All of the membranes were stabilized for the PWP measurement for 30–45 min. The water permeability of the pure PES membrane was relatively low, as shown in Table I. The addition of 10 wt % SPEEK to the casting solution provided an increase in permeability to $31 \text{ L m}^{-2} \text{ h}^{-1}$. Furthermore, at 40 wt % SPEEK in the blend, there was an appreciable increase in the permeability of the blend membrane to $86 \text{ L m}^{-2} \text{ h}^{-1}$. Other researchers reported similar results with hydrophilic polymers such as sulfonated polysulfone increasing the pure water flux of polyurethane blend membranes.²⁵ As PES is a relatively hydrophobic polymer, its water permeability is poor. Because of its high hydrophilicity and negative charges, SPEEK was used as a blend polymer to increase the hydrophilicity of PES and enhance water permeability. Because of the electrostatic repulsion between SPEEK molecules, the addition of SPEEK in a casting solution impedes the bundling of polymers, which can give rise to larger pore sizes or interconnected pores. Therefore, the systematic addition of SPEEK was expected to greatly increase PWP. These data show the important role of SPEEK in the control of the membrane morphology.

Water content

The prepared blend membranes were subjected to a water content study, and the results are shown in Table I. The PES membrane, in the absence of SPEEK, was found to have a water content of 70%. In the PES/SPEEK polymer blend, as the SPEEK content was increased, the water content also increased, and at 40 wt % SPEEK, the water content was found to be 89%. Similar results were also observed for cellulose acetate and sulfonated polysulfone blend UF membranes.²⁶ The water content actually represents the fraction of water molecules occupied in the pores of the membrane. In this study, the enrichment of the hydrophilic polymer was expected to increase the

water content at the membrane surface. An increase in the water content indicated that the membrane became more porous. With progress in gelation, the diffusion of the hydrophilic polymer was prohibited, and most of the hydrophilic polymer was fixed in the surface layer of the solidified membrane.²⁷ As a result, the concentration of the hydrophilic polymer in surface layer was higher than that in matrix. Concerning the specific phase-inversion process, this enrichment should also have taken place at the walls of the internal pores. The increased water content confirmed the enhanced PWP and porosity of the PES/SPEEK blend membranes.

Porosity

The porosity of the PES/SPEEK blend membranes is shown in Table I. The increase in the concentration of SPEEK resulted in a significant improvement in the porosity of the PES/SPEEK blend membranes. Under the preparation conditions applied in this study, the introduction of the SPEEK polymer into pure PES increased the porosity of the surfaces and bulks of the blend membranes. The SPEEK polymer remained in the formed membrane after the gelation process in the coagulation bath and was substantially enriched at the membrane surface. This enrichment resulted in a membrane surface with a much better hydrophilicity than that of the pure PES membrane, which was confirmed by PWP measurements. The increased porosity may be explained on the basis of thermodynamic or kinetic considerations. The addition of hydrophilic polymer into the casting solution may have had two effects opposite to each other. First, it could have caused the thermodynamic enhancement of the phase separation by reduction of the miscibility of the casting solution with the nonsolvent; this would have resulted in instantaneous demixing. Alternatively, it could also have caused kinetic hindrance against phase separation through an increase in the viscosity of the solution; this would have resulted in delayed demixing.^{28–30} Thus, in this study, the increase in porosity in the membranes with SPEEK may have been due to a decrease in the miscibility of the casting solution with water with the addition of SPEEK. This, in turn, could have worked in favor of the thermodynamic enhancement of phase separation and resulted in the demixing of the casting solution. This was also reported by Chakrabarty et al.³¹ in their study with polyethylene glycol (PEG) and polysulfone (PSf) to substantiate the increased porosity.

Membrane hydraulic resistance

Membrane hydraulic resistance indicates the tolerance of a membrane to hydraulic pressure. The

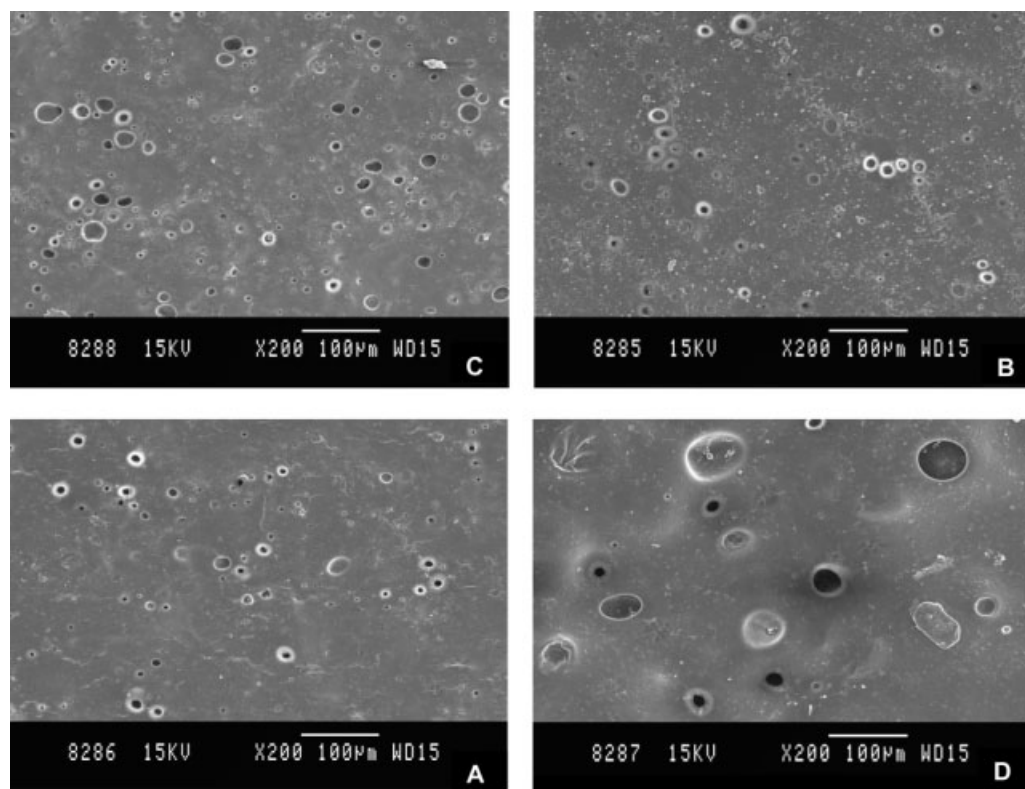


Figure 2 Scanning electron microscopic images showing the surface view of PES/SPEEK blend membranes: (A) 100/0 wt % (B) 90/10 wt % (C) 80/20 wt % (D) 70/30 wt %.

variation of pressure or the intermediate pressure ranges are important conditions to be studied for UF operations.³² The membrane hydraulic resistances of the membranes were calculated from the inverse of slopes of the corresponding flux versus pressure lines and are shown in Table I. It is evident from Table I that the pure PES membrane, in the absence of SPEEK, exhibited a higher membrane resistance of $13.6 \text{ kPa/L m}^{-2} \text{ h}^{-1}$ because of its low porosity. As SPEEK composition increased from 10 to 40%, the hydraulic resistance decreased gradually from 9.6 to $2.7 \text{ kPa/L m}^{-2} \text{ h}^{-1}$. The decrease in membrane resistance may have been due to the presence of SPEEK in the blend, which formed a segmental gap between PES, which could have been directly related to the reduction in resistance toward hydraulic pressure.³³

Morphological studies

SEM images showing the top surfaces of the pure and blend PES membranes are shown in Figure 2. The pure PES membrane had a dense separation surface with micropores. When SPEEK was added to the casting solution, more micropores appeared at the membrane surface. The size of such pores on the membrane surface increased as the SPEEK content in the blend membrane increased, as is evident in Figure 2(C,D). The pore formation of the top surface

was possibly due to demixing of the casting solution by means of the nucleation and growth of the polymer-rich phase, that is, the solid phase.^{31,34} This resulted in nodule/aggregate formation on the surface, which led to much better interconnected pores. These results were in agreement with the porosity data. Cross-sectional views of the prepared membranes are shown in Figure 3. As presented in Figure 3(A), membranes that were prepared from casting solutions with a 100/0 wt % PES/SPEEK polymer concentration exhibited a thicker skin layer and a finely porous support layer that intended to promote more selective but less productive asymmetric membranes for the UF process. On the other hand, membranes produced from casting solutions with a polymer concentration of 90/10 wt % PES/SPEEK [Fig. 3(B)] showed a thin skin layer and uniform large voids throughout the support layer. Similar types of structures were reported in the case of ultrathin-skinned asymmetric polysulfone membranes for gas-separation processes.³⁵ Furthermore, as illustrated in Figure 3(D), membranes prepared from a 70/30 wt % PES/SPEEK ratio resulted in a relatively thin skin layer and a large porous support layer with porosity gradually progressing from the top to the bottom layer of the membrane. Membranes produced from 60/40 wt % PES/SPEEK [Fig. 3(E)] resulted in a very thin skin layer and bulbous macrovoids throughout the support layer. A similar

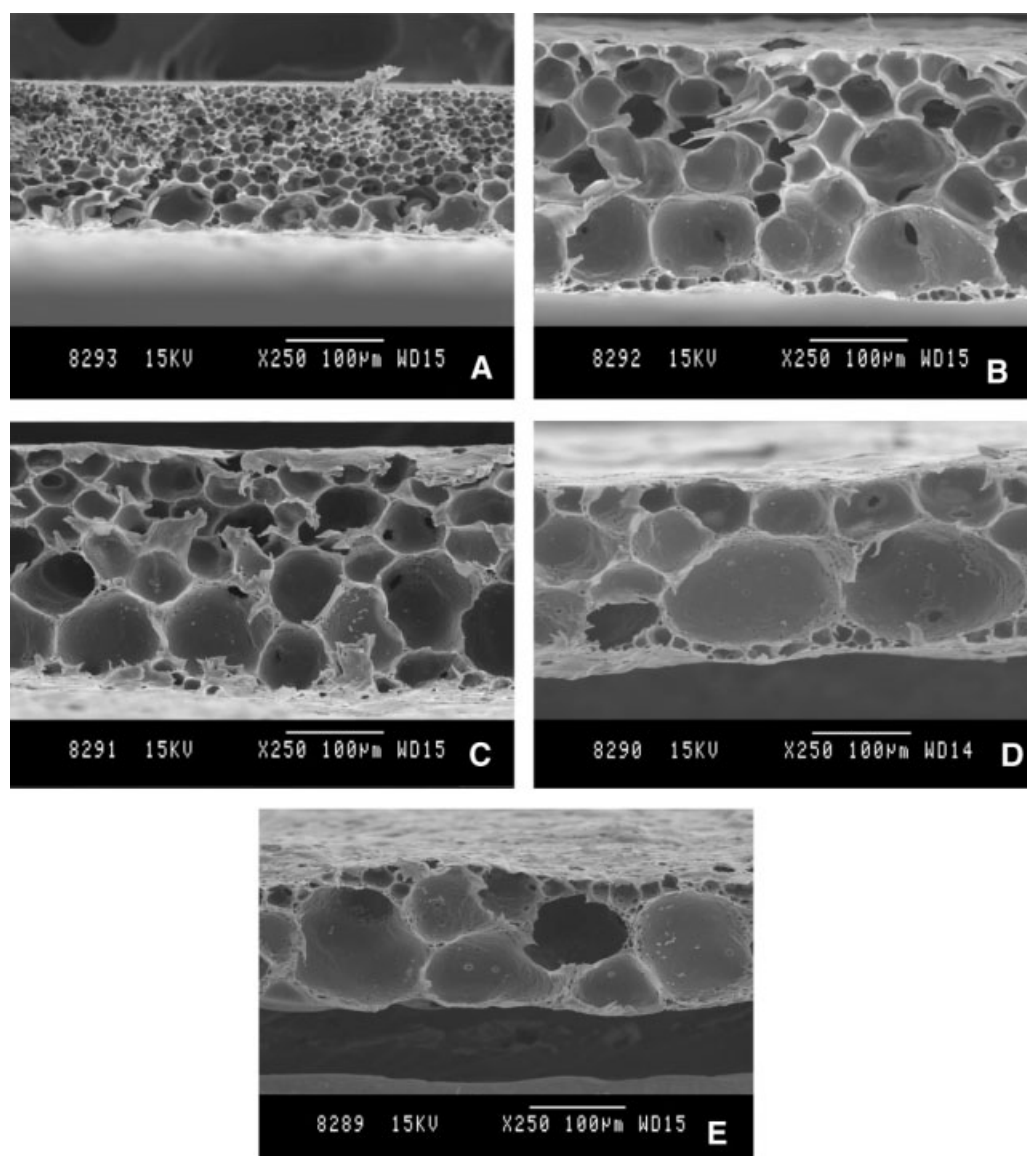


Figure 3 Scanning electron microscopic images showing the cross section view of PES/SPEEK blend membranes. (A) 100/0 wt % (B) 90/10 wt % (C) 80/20 wt % (D) 70/30 wt % (E) 60/40 wt %.

type of observation was also reported by Wang and Li³⁶ when they prepared PES hollow-fiber gas-separation membranes. The increase in the composition of SPEEK in the casting solution led to the formation of small and uniform pores beneath the external skin layer. Nonetheless, membranes with 60/40 wt % PES/SPEEK led to the formation of macrovoids in the support layer, which provided high permeability and, consequently, led to relatively low separation in the UF processes. These results were in agreement with the observations made for the SEM analysis of the membrane surfaces and with the porosity data.

DSC measurements

Figure 4 shows the DSC thermograms for pure PES and select PES/SPEEK blend membranes with dif-

ferent compositions. The DSC results show that the first melting of the pure PES membrane was around 95.29°C, which may have been due to the evaporation of solvent. Other melting curves were not noticed because the analysis was not carried out at a higher temperature range. Pure SPEEK has a glass-transition temperature greater than 200°C, which was reported previously.^{10,37} When the SPEEK was introduced into the PES membrane, the melting temperature of the blend membranes decreased to a lower temperature range because of the SO₃H interactions, which could hinder the mobility of the polymer chain.^{38,39} The melting temperature of the PES/SPEEK membrane with 10 wt % SPEEK content was 84.89°C. The melting temperature was further decreased to 82.51 and 80.22°C for membranes with 20 and 30 wt % SPEEK contents, respectively. The

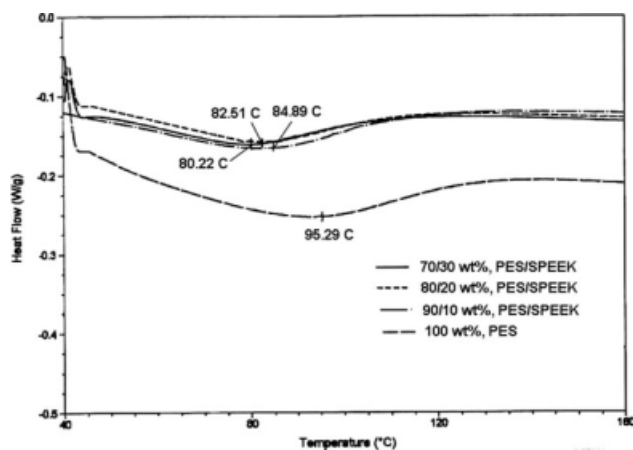


Figure 4 DSC thermo grams of PES/SPEEK membranes.

depression of melting temperature for blend membranes in comparison with pure PES suggested the occurrence of intermolecular interactions between PES and SPEEK, which may perhaps have suppressed the formation of crystalline components in the blend membrane. The appearance of a single melting temperature in the blend membranes suggested that the PES and SPEEK were mixed homogeneously with high compatibility.⁴⁰

Separation of the protein solution

Effect of the concentration of SPEEK on the permeate flux

The effect of the concentration of SPEEK on the protein solution permeate flux through various PES/SPEEK blend membranes is shown in Figure 5. It was apparent that the permeate flux of a given protein through the PES/SPEEK blend membranes was higher than that through the pure PES membrane. As the SPEEK concentration increased in the casting solution, the permeate flux for all of the proteins increased. The permeate flux of trypsin for the pure PES membrane was found to be $1.6 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ and for the membrane prepared from the casting solution having 40 wt % SPEEK, the permeate flux increased to $23 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$. This was because, as the concentration of SPEEK in the casting solution increased, the porosity of the membranes also increased.⁴¹ Similar trends were observed for the pepsin, EA, and BSA protein solutions. SPEEK is a charged polyelectrolyte; it is possible that electrostatic repulsion will hold up the bundling of polymers, which could give rise to larger pores or interconnected pores. Therefore, the systematic addition of SPEEK could be expected to greatly increase the pore size, as we found experimentally. We observed that the permeate flux increased rapidly for all of the proteins when the concentration of

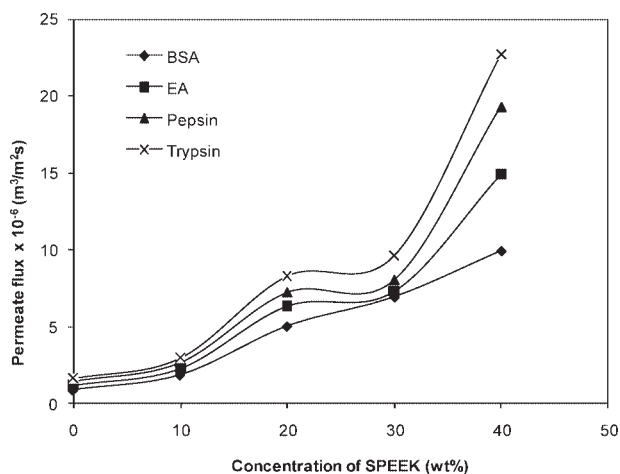


Figure 5 Plot showing the effect of concentration of SPEEK on permeate flux of proteins.

SPEEK increased from 30 to 40 wt % in the casting solution. This was in agreement with the morphological structure and pure water flux results for the increase in concentration of SPEEK from 30 to 40 wt % in comparison to other systematic increases, as shown in Table I. The order of magnitude of permeate flux of the protein solutions was found to be Trypsin > Pepsin > EA > BSA for all of the membranes; this was due to the differences in the molecular weights. The lowest permeate flux was observed for BSA at a 0 wt % SPEEK concentration, which was $0.88 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$.

Effect of the concentration of SPEEK on rejection

The effects of the concentration of SPEEK on the percentage rejection of proteins for all of the PES/SPEEK blend membranes are shown in Figure 6. In general, an increase in the concentration of SPEEK resulted in a decrease in the percentage rejection of

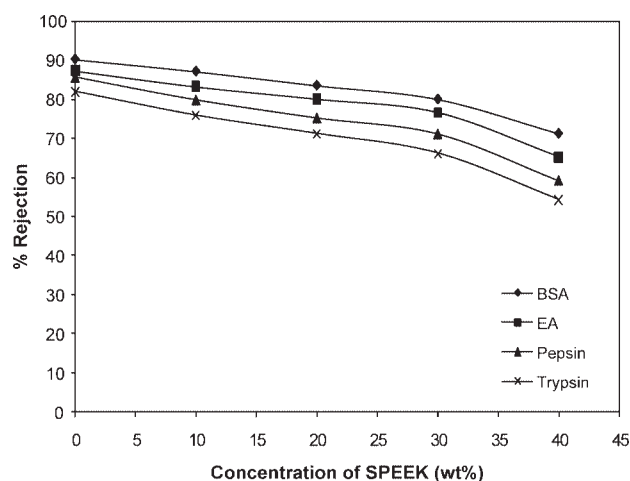


Figure 6 Plot showing the effect of concentration of SPEEK on rejection of proteins.

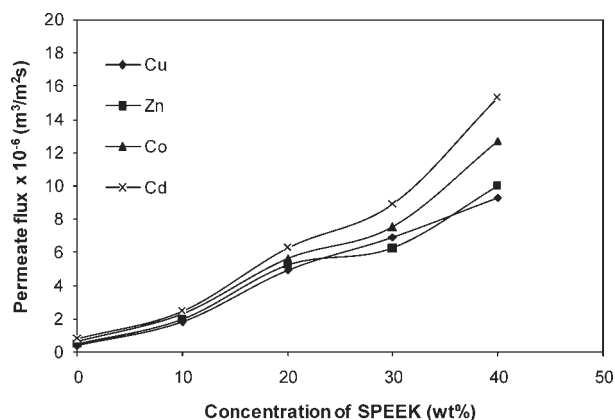


Figure 7 Plot showing the effect of concentration of SPEEK on permeate flux of metal ions.

all of the proteins. The rejection of trypsin for the pure PES membrane was found to be 82%, whereas for the membranes prepared from the casting solutions having 10–40 wt % SPEEK, the rejection decreased up to 53%. Similar trends were observed for the rejection of pepsin, EA, and BSA. The decreasing trend of rejection as the concentration of SPEEK increased was due to the fact that the porosity of the membrane increased as the concentration of SPEEK in the casting solution increased, as revealed by the morphology and other results. Interestingly, the extent of rejection was on the order of BSA > EA > Pepsin > Trypsin for all of the membranes. This was because BSA had a higher molecular weight compared to the other three proteins, and trypsin had a lower molecular weight compared to BSA, EA, and pepsin. In general, it seemed that the trend was reverse that observed for the permeate flux of the proteins.

Removal of metal ions

Effect of the concentration of SPEEK on the permeate flux

The permeate flux values of the metal-ion solutions on increasing concentrations of SPEEK in the PES/SPEEK blend membranes are shown in Figure 7. The permeate flux values of all of the metal ions increased as the concentration of SPEEK increased in the casting solution. The permeate flux of Cu(II) for the pure PES membrane was $0.45 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$, whereas for the membrane prepared from the casting solution having 40 wt % SPEEK, the permeate flux increased to $10.2 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$. There was a rapid increase in the permeate flux of all of the metal ions as the concentration of SPEEK in the casting solution increased beyond 30 wt %, as observed during protein-removal studies. The permeate flux of Cu(II) was lower than those of the

other metal-ion solutions, and the order of the permeate flux was Cd(II) > Co(II) > Zn(II) > Cu(II). This was because Cu(II) had a higher affinity for N-donor ligands compared to Cd(II) and Zn(II).⁴² Hence, it was possible that Cu(II) could have easily formed more macromolecules than other metal ions chosen in this study. This led to the reduced permeate flux for Cu(II) and enhanced the rejection. Hence, the extent of removal of the metal ion depended on the formation of macromolecules with the PEI complexing agent and on the morphological structure of the membranes.

Effect of the concentration of SPEEK on rejection

The effects of the concentration of SPEEK on the percentage rejection of metal ions for the PES/SPEEK blend membranes are shown in Figure 8. In general, permeate flux and rejection possess an inverse relationship, as seen in protein-removal studies. Similar to the observations made in the protein-rejection studies, the increase in the concentration of SPEEK resulted in a decrease in the rejection of all of the metal ions. The rejection of Cu(II) for the pure PES membrane was 92% and for the membrane prepared from a casting solution having 40 wt % SPEEK, the rejection decreased to 67%. The rejection of Cd(II) for the pure PES membrane was 85%, and this value was lower than that of Cu(II). Similar observations were also found for the rejection of other metal ions, such as Zn(II) and Co(II). The rejection of Cu(II) was found to be higher than that of other metal ions for all of the membranes, and the order of rejection was Cu(II) > Zn(II) > Co(II) > Cd(II). This may have been due to the higher binding ability of Cu(II) with PEI. It has been shown that Cu(II) has a higher complexation constant compared to Zn(II) and Cd(II).⁴³

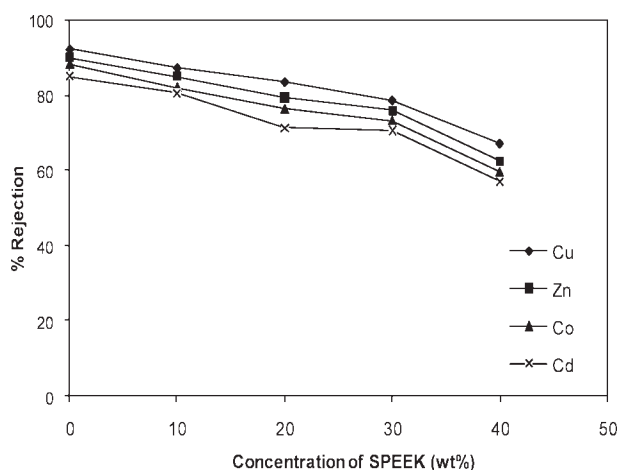


Figure 8 Plot showing the effect of concentration of SPEEK on rejection of metal ions.

Furthermore, it is known that Zn(II) and Cd(II) complexes have low ligand-field stability because of the complete filling of *d* orbitals. Similar observations on the higher rejection of Cu(II) compared to Zn(II), Ni(II), and Cd(II) with PEI as a complexing agent were reported by Mandel and Leyte.⁴⁴

CONCLUSIONS

In this study, PES as a base polymer was blended with SPEEK contents ranging from 0 to 40 wt % with DMF as the solvent to prepare modified PES membranes. Polymer solutions having SPEEK concentrations greater than 50 wt % did not form membranes. The characterization of the prepared membranes illustrated that the pure water flux and water content increased whereas the membrane hydraulic resistance decreased as the concentration of SPEEK in the casting solution increased. The SEM study showed a continuous increase in the pore size in the support layer and a subsequent decrease in the thickness of the skin layer as the concentration of SPEEK in the casting solution increased, which was supported by porosity data. The rejection of proteins was on the order BSA > EA > Pepsin > Trypsin, which was directly proportional to the molecular weights of the proteins. The extent of rejection of metal ions followed the order Cu(II) > Zn(II) > Co(II) > Cd(II), which depended on the complexation ability to form macromolecules and ligand-field stability of the individual metal ions. The results suggest that both the protein and metal-ion removal involved a sieving mechanism influenced by the molecular weight of the solute and the porosity of the membranes. The blending of SPEEK with the PES polymer matrix resulted in substantially high permeability and a reduction in the membrane resistance properties; this led to a significant improvement in the flux and a marginal reduction in the rejection.

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