

Sulfonated Polyethersulfone by Heterogeneous Method and Its Membrane Performances

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Received 9 November 1998; accepted 15 May 1999

ABSTRACT: Polyethersulfone was sulfonated by heterogeneous method with chlorosulfonic acid. Ion exchange capacity was controlled to 0.68 meq/g to reduce fouling. Sulfonation was confirmed by Fourier transform infrared spectroscopy and ^1H -nuclear magnetic resonance. Polyethersulfone and sulfonated polyethersulfone ultrafiltration membranes were prepared successively by the typical phase inversion method. Membrane performance of sulfonated polyethersulfone was compared with that of polyethersulfone. In the preparation of ultrafiltration membranes, the effect of the addition of dichloromethane and poly(vinyl pyrrolidone) in a casting solution was investigated on the membrane performance. It was observed that the addition of dichloromethane increased the solute rejection rate. By changing the ratio between polymer and poly(vinyl pyrrolidone), membrane performance could be controlled. Negatively charged sulfonated polyethersulfone could reduce fouling at higher or lower pH than isoelectric point of protein bovine serum albumin. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2046–2055, 1999

Key words: sulfonated polyethersulfone; fouling; ultrafiltration membrane

INTRODUCTION

Ultrafiltration (UF) is a very versatile and widely used separation process for fractionation, purification, separation, and concentration of water soluble macromolecules. UF membranes, with pore size typically ranging from 0.05 μm to 1 μm are capable of retaining species in the molecular weights of a few thousand daltons. Applications can be found in fields such as the food and dairy industry, pharmaceutical industry, textile industry, chemical industry, metallurgy, paper industry, and leather industry. Various applications in the food and dairy industry are the concentration of milk and cheese making, the recovery of whey proteins, the recovery of potato starch and proteins, the concentration of egg products, and the

clarification of fruit juices and alcoholic beverages.

One of the serious limitations encountered in UF is a continuous permeation flux decrease, which affects both solute-solvent and solute-solute separations. The flux decline is generally expressed as fouling. The actual mechanism of the fouling that occurs due to protein adsorption, aggregation, and denaturation is not well understood. The negative effects on performance due to the fouling are basically known. The adsorption of solutes onto solid surfaces can be attributed to different types of interactions—hydrophobic interactions, H-bonding, van der Waals interactions, and electrostatic effects, for example.^{1–4}

Various means are used to minimize this unwanted phenomenon. They are either operational procedures applied during the UF process or membrane material modification. Most of the commercially available membrane materials, polysulfone and polyethersulfone (PES), etc., are

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Journal of Applied Polymer Science, Vol. 74, 2046–2055 (1999)

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CCC 0021-8995/99/082046-10

hydrophobic. This hydrophobic character is widely believed to be correlated with protein fouling. Numerous attempts have been undertaken to modify membrane materials to produce membranes less susceptible to fouling. There were many investigations to modify polysulfone using sulfur trioxide or chlorosulfonic acid.^{5–8} PES is a closely related derivative of polysulfone which is totally devoid of aliphatic hydrocarbon groups and has a higher glass transition temperature of 230°C.⁹ It is an excellent UF membrane material because of its film and membrane forming properties and high mechanical and chemical stability, in addition to being commercially available and relatively inexpensive. It is thus one of the most widely used polymers for making UF membranes. An improved PES UF membrane with less susceptibility to fouling would have strong economic impact on the membrane industry. However, the modification of PES was known to be more difficult than polysulfone. Therefore, most of the modification attempts have been focused on polysulfone.

The objective of this work is to develop a modified PES UF membrane using a more economic and effective heterogeneous slurry sulfonation method. With the modified polymer, we investigated the effects of nonsolvent and pore-forming agent in casting solution on the membrane performance and fouling susceptibility of membranes.

EXPERIMENTAL

Materials

Ultrason PES (BASF, Ludwigshafen, Germany) were dried at 130°C for 10 h. Chlorosulfonic acid (CSA), dichloromethane (DCM), *N*-methyl-2-pyrrolidone (NMP) and poly(vinyl pyrrolidone) (PVP) (molecular weight 10,000 Da) were purchased from Aldrich Chemical (Milwaukee, USA) and used without further purification. Protein bovine serum albumin (BSA, Sigma, Milwaukee, USA) for fouling test was used without further purification.

Sulfonation by Slurry Method

Similar to procedures described by Coplan and Gotz,⁹ the dried PES (30 g, 0.129 mols/repeating unit) was dispersed in 70 mL DCM. This solution was stirred vigorously at room temperature. We

prepared slurry by changing the amounts of DCM and stirring speed. The resulting slurry formation was dependent on the amounts of DCM and stirring speed. Slurry was insoluble in DCM. That means solubility character of PES was changed. After slurry formed more 100 mL DCM was added in the reaction flask. Then the slurry was heated to 40°C with continuous stirring. Five milliliters of CSA in 100 mL of DCM was added dropwise under dry nitrogen within 1 h to the vigorously stirred slurry with reflux. The resulting reaction mixture was stirred for an additional 6 h. The top DCM layer was decanted and the isolated precipitate was washed with fresh DCM and dried at 70°C for 10 h. Sulfonated PES (SPES) obtained was purified in hot water to remove small molecular weight water soluble polymer.

Polymer Characterization

The formation of sulfonic acid groups was detected using Fourier transform infrared (FTIR) spectroscopy (films, Digilab model FTS-60) and ¹H-nuclear magnetic resonance (¹H-NMR) spectroscopy (Varian Unity 300, solvent: deuterated DMSO). The degree of sulfonation was measured quantitatively via the ion exchange capacity (IEC). SPES, 1 g, was soaked in 50 mL 0.1N NaOH for 1 day. The converted SPES with Na ion was filtered off. The remaining 20-mL solution was titrated with 0.1N HCl using the autotitrator according to the procedure described by Fisher and Kunin.¹⁰ In addition to titration FTIR¹¹ and ¹H-NMR¹³ spectroscopy, evaluating aromatic proton signals were used. Inherent viscosity was measured in 0.5 g/dL NMP solution at 30 ± 0.1°C with an ubbelohde viscometer.

Cloud Point and Tie-Line

Polymer solutions with different compositions (1, 3, 6, 10, and 15%) were placed in tubes at 30°C. In the case of polymer solutions with small polymer compositions (1 and 3%), distilled water was added slowly until turbidity occurred. Water/NMP (4 : 1) was added to other polymer solutions (6, 10, and 15%) until turbidity occurred.¹⁷ The composition at the onset of turbidity, the so-called cloud point, represents the transition concentration between the one-phase and two-phase regions. The cloud point curve can be interpreted as the binodal curve in a ternary phase diagram.¹⁸

Alliquots of a polymer/NMP/water mixture at its cloud point composition were kept at 25°C in a

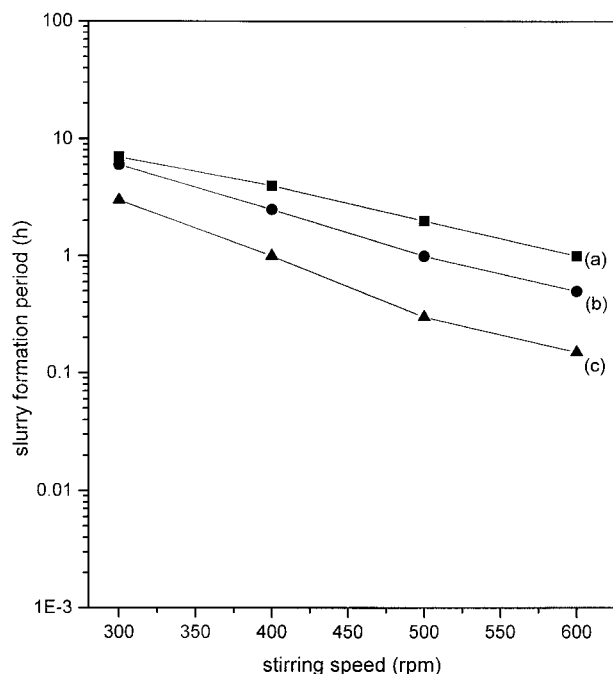


Figure 1 Slurry formation period on various stirring speeds and polymer solution concentrations (a) PES 10 wt % in DCM; (b) 20 wt %; (c) 30 wt %.

thermostated bath for more than a month. The turbid polymer solutions developed two clear liquid layers. The less viscous top layer was withdrawn. The water content in this mixture was determined by gas chromatography. The polymer content of the upper phase was determined from the weight after evaporation to dryness. But the top and bottom layers were removed separately and dried for 2 days until constant weight of the polymer residue was observed. Tie-line compositions were then calculated through material balance.^{18,19}

Membrane Preparation

Flat sheet phase inversion membranes were prepared by casting solution that consisted of PES (SPES), NMP, DCM, and PVP with a casting knife of 200 μm on top of a nonwoven polypropylene support. Before immersing into the coagulation bath, the proto membrane remained for 30 s in ambient air of 60 to 65% relative humidity. The precipitation bath consisting of pure water was kept at a temperature of 4°C. All membranes were stored in distilled water until used. The casting solution compositions were controlled by adding nonsolvent DCM and pore-forming agent

additive PVP. SPES concentration was fixed as 23 wt %.

Membrane Investigations

Flat sheet membranes were tested using a batch-type cell. This cell was used to measure characteristics of various membranes quickly and to find the best casting condition. Molecular weight cut-off values were measured using poly(ethylene glycol) (PEG) of molecular weights 20,000 Da supplied by Wako (Oajudo, Japan). The solute concentrations in the feed and the permeate were determined by high performance liquid chromatography (Waters 410) measurements. The solute rejection R is defined as

$$R(\%) = (1 - C_p/C_f) \times 100$$

where C_p and C_f are the PEG concentration in the permeate and the feed, respectively.

This cell was also used to investigate the effect of charge on the plugging characteristics of membranes using bovine serum albumin at different pH values. Testing conditions were as follows:

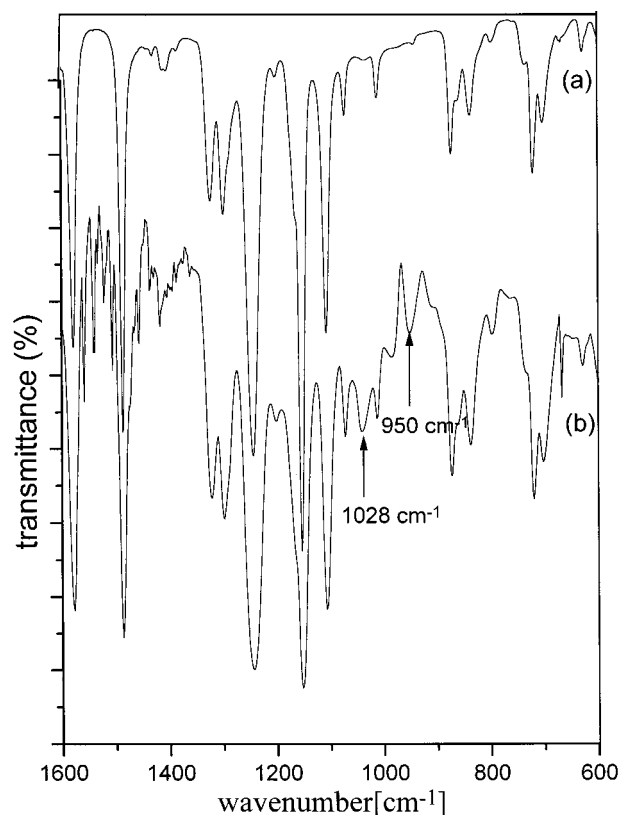


Figure 2 FTIR spectra of (a) PES, and (b) SPES-2.

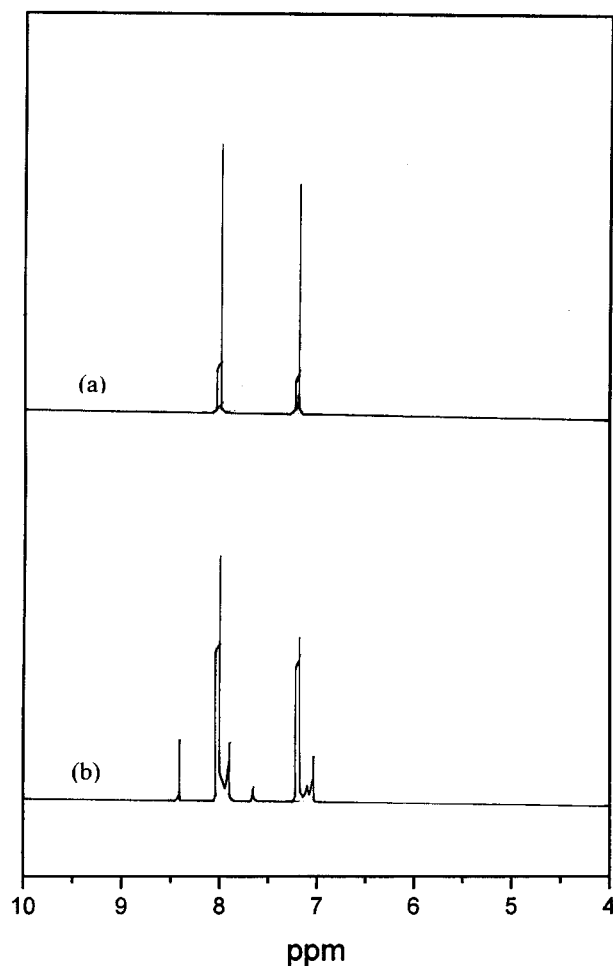


Figure 3 $^1\text{H-NMR}$ spectra of (a) PES, and (b) SPES-2.

temperature, 25°C ; flow rate, 2.5 L/min; pressure, 1 kgf/cm^2 . Concentrations were below 500 ppm to prevent gel layer formation on the membranes. Cross sections of the precipitated membranes were observed by using scanning electron microscopy (SEM) (JSM-5410LV). Air-dried membrane samples were fractured under cryogenic conditions using liquid nitrogen. The fractured membranes were coated with gold before SEM photographs were taken.

RESULTS AND DISCUSSION

Slurry Sulfonation

The polymer PES has been known to be crystallized from DCM involving formation of a mixed polymer/solvent intercrystalline structure. After a few hours, the polymer was precipitated to form

a slurry. Figure 1 shows slurry formation period depending on the stirring speeds and polymer solution concentrations. The higher the stirring speed and polymer solution concentration, the faster the slurry formation. After the well-dispersed slurry was completely formed, more DCM was poured and then CSA solution having various concentrations was added dropwise under dry nitrogen within 1 h. After reaction was completed, sulfonated polymer was filtered and dried. Almost all the sulfonation reaction has been known to form a brownish gel. Therefore, gelled polymer must be precipitated in nonsolvents such as methanol and washed with excess water to obtain sulfonated polymer. It is not an economical method. In our work, polymer did not need to be precipitated into methanol and washed with excess water. Furthermore, decanted DCM can be reused to make PES slurry. That means a highly economical method.

Polymer Properties of SPES

Figure 2 shows the FTIR spectroscopy of modified polymer. FTIR spectroscopy shows the appearance of the absorption peaks of sulfonic acid groups. It has been known that the symmetrical and asymmetrical stretching vibrations of sulfonic acid groups appear at 1028 and 1180 cm^{-1} , respectively. Another characteristic absorption peak was observed at 950 cm^{-1} . However, we could observe sulfonic acid group only at 1028 and 950 cm^{-1} . Polymers with three different degrees of sulfonation were prepared and characterized. The degree of sulfonation was determined quantitatively via the titration method, FTIR, and $^1\text{H-NMR}$ spectroscopy. The FTIR method could be used to obtain the degree of substitution, on the basis of the $-\text{SO}_3^-$ stretching peak at 1028 cm^{-1} . This absorption peak was compared against internal standard aryl ether unit. $^1\text{H-NMR}$ method was also used to assess the degree of sulfonation.

Table I Ion Exchange Capacity Differences and Viscosity Changes of Sulfonated PES

	PES	SPES-1	SPES-2	SPES-3
Viscosity (dL/g)	0.32	0.34	0.38	0.41
Titration (meq/g)	—	0.21	0.48	0.61
FTIR (meq/g)	—	0.24	0.52	0.66
$^1\text{H-NMR}$ (meq/g)	—	0.26	0.53	0.69
Average value (meq/g)	—	0.24	0.51	0.65

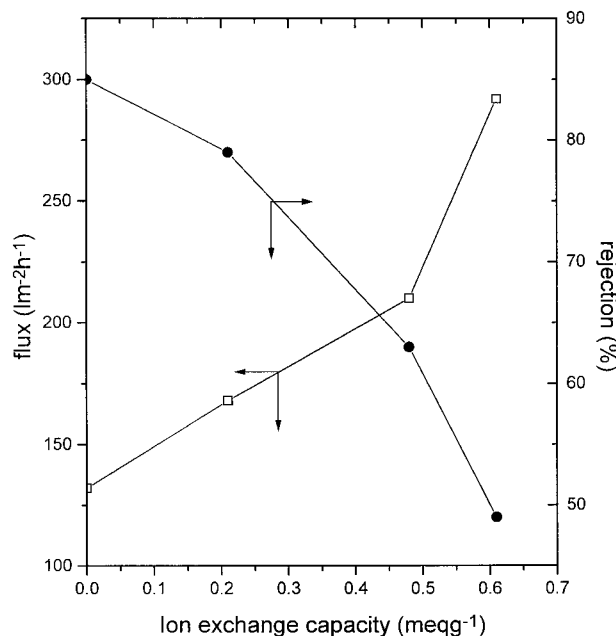


Figure 4 Membrane performance changes with IEC (casting solution composition: polymer/NMP = 23:77).

As shown in Figure 3, the presence of a sulfonic acid group causes a significant down-field shift from 7.2 to 8.3 ppm of the hydrogen located in the σ -position at the aromatic ring.¹¹⁻¹³ The incorporation of sulfonic acid functional group which can form strong hydrogen bonds is expected to increase viscosities of SPES with increasing degree of sulfonation as described for sulfonated polysulfone by Noshay and Robeson.¹⁴ However, if the polymer is degraded by sulfonating reaction, viscosities are lower. Table I shows the viscosities and IEC changes by sulfonation. As the degree of sulfonation increased, the viscosities in dilute polymer concentration increased because of the electrostatic repulsion effects. There were many IEC differences by various characteristic methods. In titration method, ion was exchanged only on the surface. Therefore, the IEC obtained was smaller than that of FTIR and ¹H-NMR methods. As shown in viscosity changes, our reaction conditions could incorporate the sulfonic acid groups at aromatic ring without degradation.

The Characteristics of UF Membranes

Figure 4 shows the membrane performance changes with IEC. Polymer concentration was fixed as 23% by weight. Rejection changes were tested with PEG 20,000. Increasing the IEC of the polymer lead to a much higher affinity at the

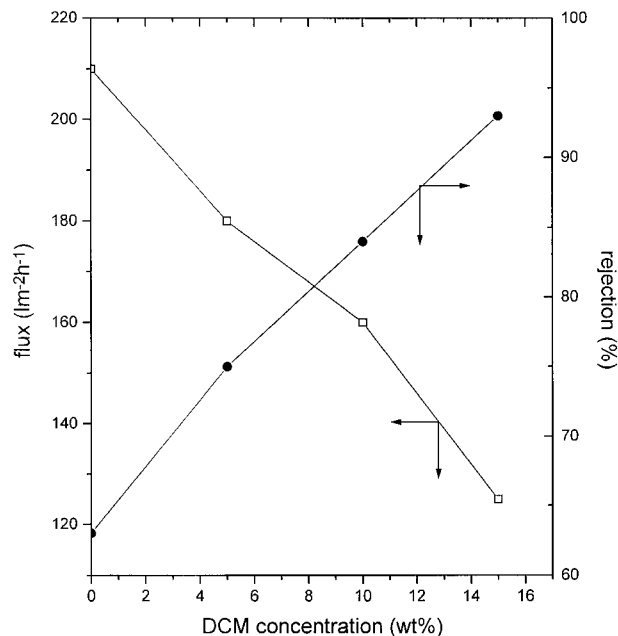


Figure 5 Nonsolvent DCM effect on SPES-2 membrane performances.

interface and resulted in more nonsolvent tolerance, implying that the miscibility between two polymers is lower. With the addition of nonsolvent, large polymer concentration fluctuation increased pore size of the membrane top layer. That means a higher permeation rate and a lower re-

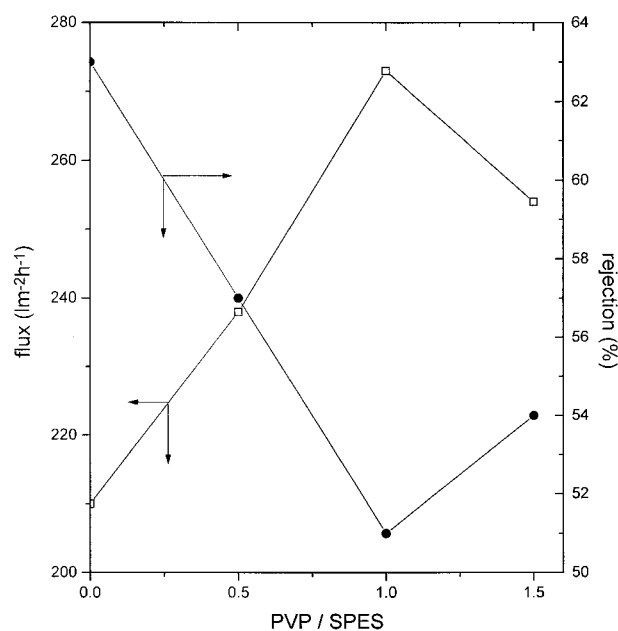


Figure 6 Pore-forming agent PVP effect on SPES-2 membrane performances.

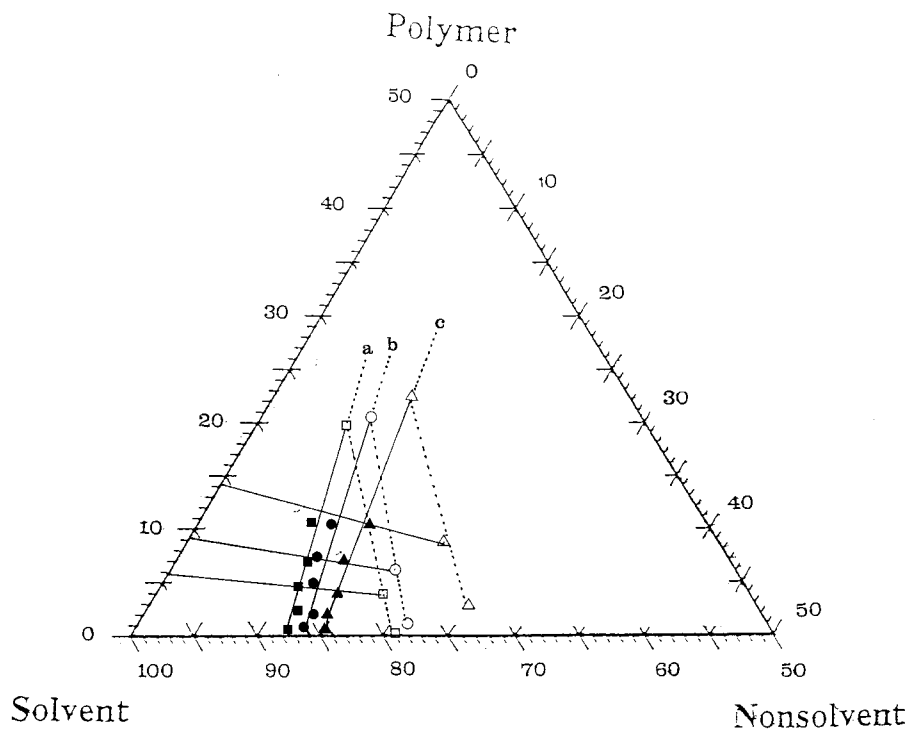


Figure 7 Phase diagram of polymer solutions with increasing the IEC (a) PES; (b) SPES-1; (c) SPES-2.

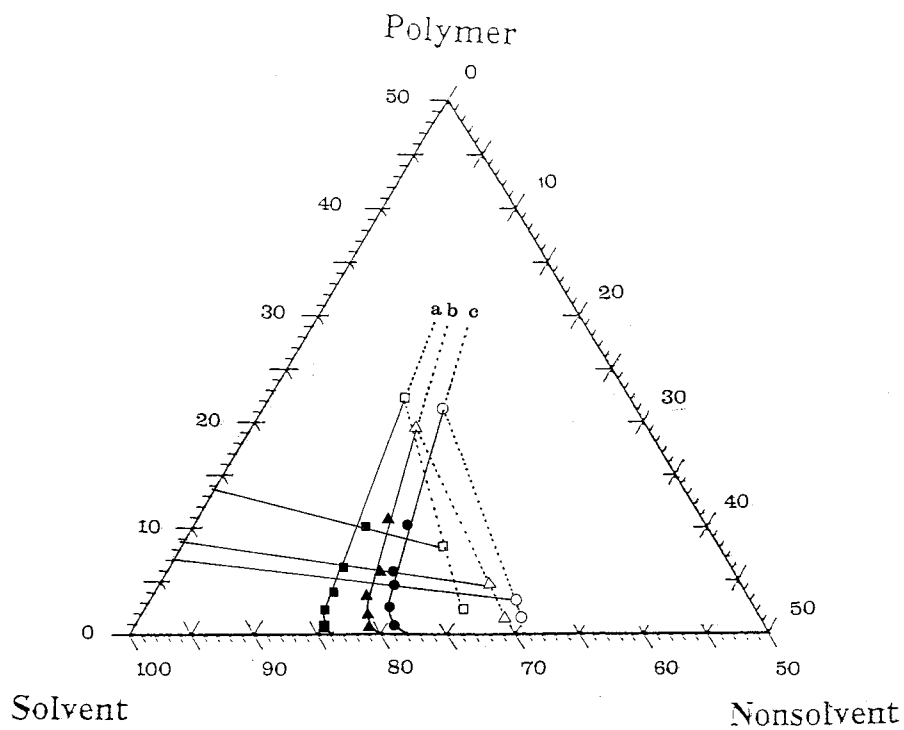


Figure 8 Phase diagram of SPES-2 solutions at different contents of PVP (a) SPES-2; (b) SPES-2/PVP = 1/2; (c) SPES-2/PVP = 1/1.

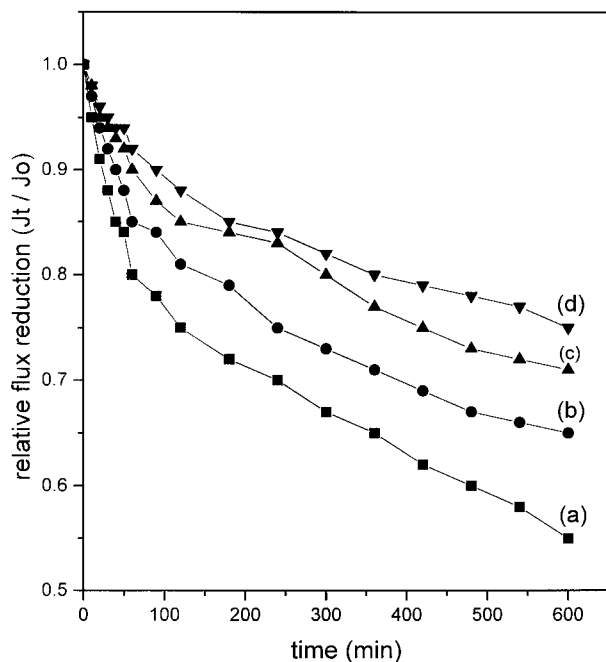


Figure 9 Fouling effect on IEC at pH 3.0 (a) PES; (b) SPES-1; (c) SPES-2; (d) SPES-3.

jection rate. When IEC was increased above 0.68 meq/g, SPES lost film-forming properties and membrane could not be prepared by the phase inversion method.

Figures 5 and 6 show the effects of nonsolvent DCM and pore-forming agent PVP, respectively, on the membrane performance. Polymer concentration was 23% by weight and rejection was tested with PEG 20,000. When membrane is cast on nonwoven fabric, DCM having low boiling point, evaporates on the membrane surface and the surface polymer concentration becomes higher and tighter. Furthermore, the addition of DCM in polymer solution results in low nonsolvent tolerance. As a result, UF membranes having a less porous top layer is obtained.

Pore-forming agent PVP has been known to blend easily with SPES. The interaction between PES and PVP was the strongest when the weight ratio was unity and the structure of the film casting solution under such a strong interaction force in the pore size distribution and, consequently, increased the permeation rate through the UF membrane.¹⁵ The

The $\text{N}-\text{C}=\text{O}$ ring in the PVP interacts with SO_2 group which is apparently the most active polar group in the SPES polymer. The concentration of SPES polymer was changed from 20 to 25% by weight, whereas keeping the weight

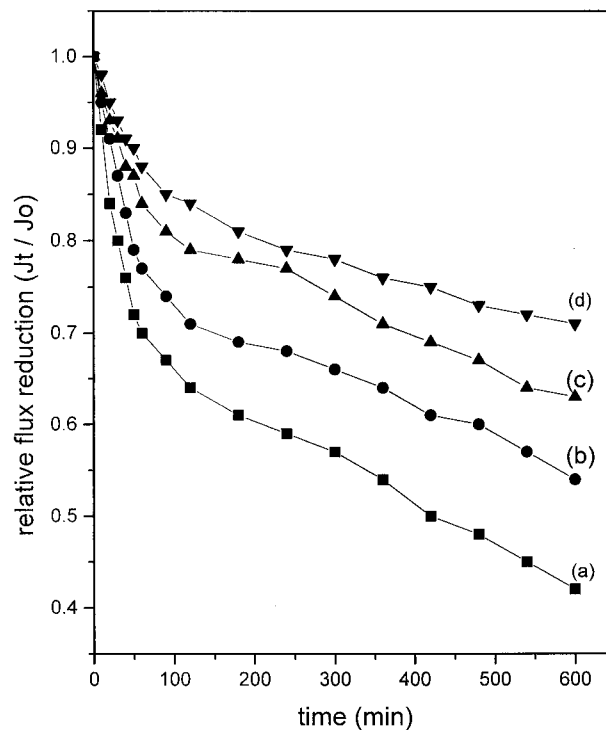


Figure 10 Fouling effect on IEC at pH 4.8 (a) PES; (b) SPES-1; (c) SPES-2; (d) SPES-3.

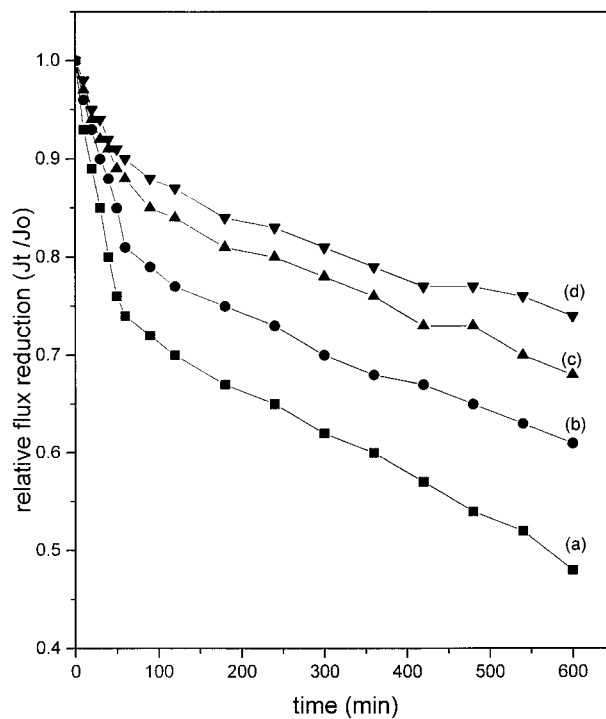


Figure 11 Fouling effect on IEC at pH 8.0 (a) PES; (b) SPES-1; (c) SPES-2; (d) SPES-3.

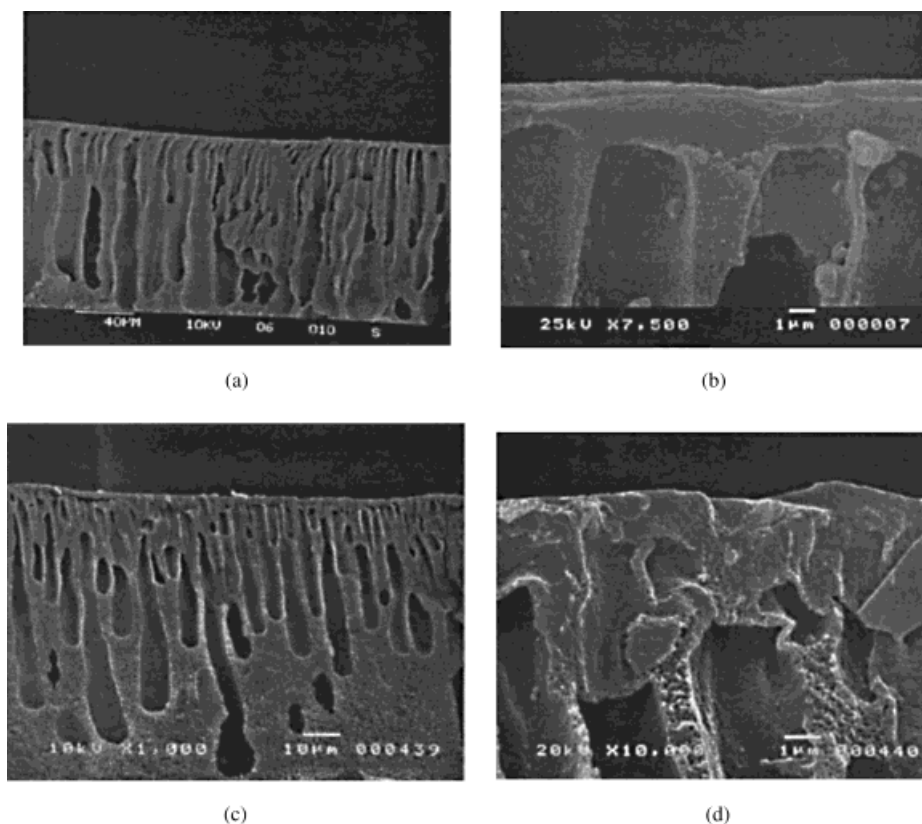


Figure 12 SEM photographs (a) cross-section of 23 wt % PES membrane sublayer; (b) cross-section of 23 wt % PES membrane skin layer; (c) cross-section of 23 wt % SPES membrane sublayer; (d) cross-section of 23 wt % SPES membrane skin layer.

ratio of PVP and SPES in the range of 0–2. When the SPES/PVP weight ratio was 1.0, the permeation rate was the largest because of the strongest interaction force and the resulting lowest miscibility between two polymers. The phase diagrams shown in Figures 7 and 8 illustrate that the precipitation curve shifts to the right side with increasing the IEC and PVP contents, implying that the nonsolvent tolerance of the polymer solution increases. They also indicate the capacity of the polymers to associate with water while in solution. With increasing the IEC and PVP contents, the miscibility between polymer chains becomes lower. The solvents involved in polymer chains can be exchanged easily with nonsolvents. Therefore, the resulting demixing type becomes instantaneous. In general, when the instantaneous demixing occurs, the permeation rates are improved due to more open porous membrane structure formation. Usually in the gelation process, water in the gelation bath turns white because of the release of some low molecular weight PES from the film surface.¹⁶ In our work, ice cold water

during coagulation did not turn white meaning low molecular weight SPESs were dissolved out into water during purification in water. Figures 9 to 11 show the fouling effects on IEC at different pH. Proteins in water interact with and adhere to a solid surface, especially at isoelectric point (IEP). To reduce morphological properties membrane performance was controlled with DCM and PVP. If negatively charged protein is attached onto the SPES surface, the protein experiences an electrostatic repulsion with SPES. This electrostatic repulsion resulted in lower protein adsorption onto the polymer surface and reduced fouling. The relative flux reduction of SPES was lower than that of PES. It means that SPES can reduce fouling at lower pH than IEP. Figure 12 shows the cross-section comparison between PES and SPES at the same concentration. SPES membrane a has thinner surface and sharper macrovoids, implying that SPES membrane is more porous than PES membrane. Nonsolvent DCM and pore-forming agent PVP effects were also evaluated from an SEM cross-section, as illustrated in

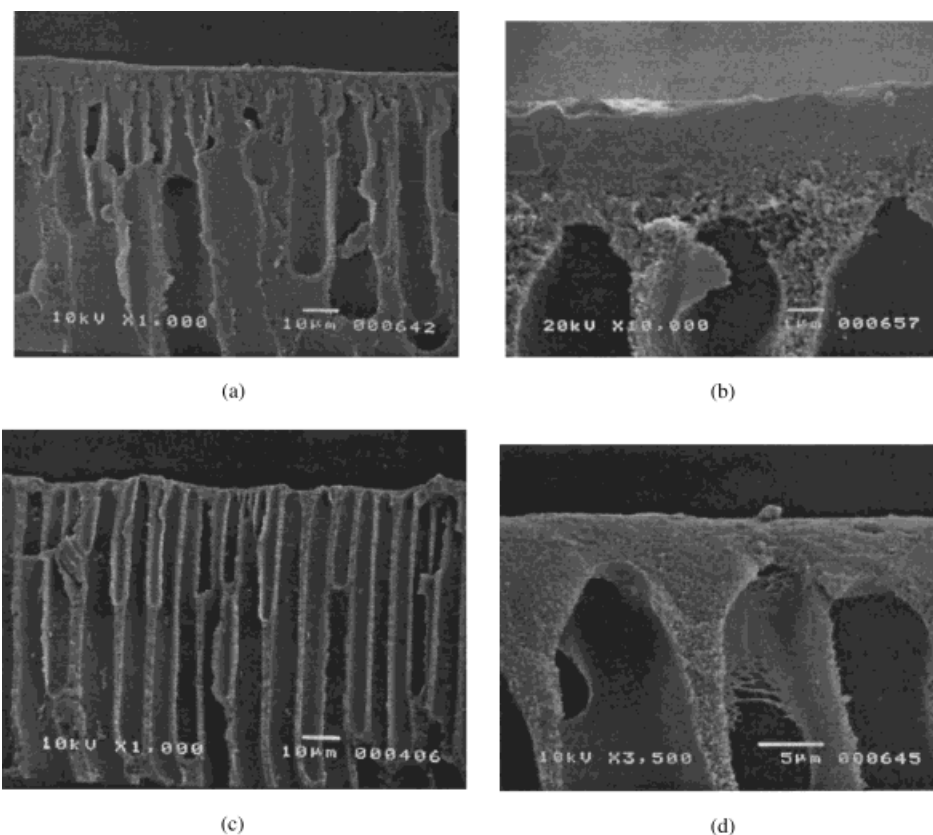


Figure 13 SEM photographs (a) cross-section of SPES membrane sublayer with 10 wt % DCM content; (b) cross-section of SPES membrane skin layer with 10 wt % DCM content; (c) cross-section of SPES membrane sublayer with PVP/SPES = 1.0; (d) cross-section of SPES membrane skin layer with PVP/SPES = 1.0.

Figure 13. This Figure shows that the nonsolvent DCM could make membrane denser because of the delayed demixing and thicker surface layer. It was known that pore-forming agent PVP made membrane more porous.

CONCLUSIONS

SPESs having various IEC were prepared by sulfonation with CSA heterogeneously. Depending on the stirring speed and polymer solution concentrations, PES precipitated to form a slurry differently. IEC could be increased to 0.68 meq/g. When IEC was increased above 0.68 meq/g, SPES lost film-forming properties and membrane could not be prepared by phase inversion method. Sulfonic acid group was confirmed by FT-IR and $^1\text{H-NMR}$. The degree of sulfonation was measured successively via titration, FTIR, and $^1\text{H-NMR}$. UF membranes were prepared by the typical phase inversion method. Increasing the IEC resulted in higher flux and lower rejection because of the high affinity between

SPES and water. A tighter membrane could be prepared by adding nonsolvent DCM in casting solution. A more porous membrane could be prepared by adding pore-forming agent PVP because of the interaction between SPES and PVP. The miscibility between polymer chains becomes lower with increasing IEC and PVP contents. That could also be revealed in the phase diagrams and SEM photographs. Fouling could be reduced by introducing sulfonic acid group in basic polymer at a higher pH than IEP, especially.

The authors are grateful to Dr. S. C. Kim, the president of the Korea Advanced Institute of Science and Technology Center Advanced Functional Polymers for the support of this work.

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