

# Preparation of Sulfonated Polysulfone/Polysulfone and Aminated Polysulfone/Polysulfone Blend Membranes

MING-HUANG CHEN, TZE-CHIANG CHIAO, and TSAI-WIE TSENG

Union Chemical Laboratories, ITRI, Hsinchu, Taiwan, ROC

## SYNOPSIS

Sulfonation and amination of polysulfone (PSf) were performed in this study to improve the hydrophilicity of PSf membranes. The sulfonated polysulfone (SPSf) and aminated polysulfone (APSf) membranes with a higher degree of reaction exhibited a higher water flux and worse mechanical strength than that of the original PSf membranes. Therefore, SPSf/PSf and APSf/PSf blended membranes were prepared in this study to improve their individual properties. By altering the formulations of casting solutions and forming conditions of the membranes (e.g., blending ratios of both polymers, additives, evaporation time, and gelation temperature), different SPSf/PSf and APSf/PSf blending membranes were prepared; and their performance in water flux and salt rejection were measured and are discussed. A difference in salt rejection was also observed between both SPSf/PSf and APSf/PSf blending membranes that rejected the various salts. Experimental results indicated that water flux increased and salt rejection decreased with an increase of the SPSf/PSf blending ratio from 1 : 9 to 2 : 1. The order of salt rejection, in which the SPSf/PSf blended membranes rejected four varieties of salts, was  $\text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{NaCl} > \text{MgCl}_2$ . Furthermore, the opposite order was obtained by the APSf/PSf blended membranes.

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## INTRODUCTION

Polysulfone membrane possesses excellent mechanical, biological, and chemical stability, as well as having an extensive operating range at temperature ( $>80^\circ\text{C}$ ) and pH value.<sup>1-13</sup> Unfortunately, the water flux of a polysulfone membrane is too low for commercial purposes, owing to its hydrophobic property.

Hydrophilicity of polysulfone has already been improved in several investigations through application of chemical modification methods.<sup>1-7</sup> Noshay and Robeson<sup>1</sup> modified polysulfone into sulfonated polysulfone with sulfonation. Jihua et al.<sup>2</sup> also performed the same procedure with chloromethylate and further quaternized the polysulfone into quaternized (aminated) polysulfone. The above-mentioned modifying methods increased the hydrophilicity of polysulfone by introducing charged groups onto polysulfone. Therefore, hydrophilic

and charged (negative or positive) polysulfones were utilized as membrane materials for reverse osmosis and ultrafiltration.<sup>1-7</sup>

In this study, sulfonated and aminated polysulfone were synthesized and used to prepare membranes by blending with original polysulfone. The effects of the formulation of casting solutions and forming conditions of membranes (e.g., blending ratios of both SPSf, or APSf and PSf, additives, evaporation time, and gelation temperature) on membrane performances are also investigated. Furthermore, the differences in salt rejection are also studied in which both SPSf/PSf and APSf/PSf blending membranes reject four varieties of salts.

## EXPERIMENTAL

### Materials

Commercial polysulfone was Udel P3500 as purchased from Union Carbide Co. Sulfonated and aminated polysulfone were obtained by the sulfon-

ation and amination of polysulfone, respectively. *N*-methyl-pyrrolidone (NMP) supplied by Fisher Co. was used as the casting solvent. The other reagents used in this experiment were of reagent grade and were not further purified.

### Synthesis of Aminated and Sulfonated Polysulfone

Dichloromethane was used as the solvent to dissolve polysulfone. The reagents of hydrogen chloride, trioxane, acetic anhydride, and zinc chloride were poured into the solution of polysulfone of 10 wt %. The mixed solution was heated, and the reaction was started. Following the reaction, the subsequent solution was diluted with *n*-methyl-pyrrolidone and was then poured into methanol to precipitate the polymer. The product, chloromethylated polysulfone, was further washed by immersing in methanol and in deionized water several times. Consequently, the chloromethylated polysulfone was dissolved in *n*-methyl-pyrrolidone and reacted with triethylamine. The final product of aminated polysulfone was obtained by precipitating, washing, and drying of the polymer. The degree of amination of aminated polysulfone was about 0.86 in our membrane preparation.

Sulfonated polysulfone was synthesized by sulfonation of polysulfone in dichloromethane using chlorosulfonic acid as the sulfonating agent at a temperature of 4°C. The resulting polysulfone sulfonic acid was neutralized with sodium methoxide/methanol solution to produce sodium salt. The degree of sulfonation of sulfonated polysulfone was around 0.65 in this study.

### Membrane Preparation

The membrane was prepared from the casting solution of polymers, which were completely dissolved in NMP with or without additives. The casting solution was spread on a reinforced nonwoven cloth into a film by using a glass bar. After allowing to stand for a predetermined evaporation time under room conditions, the film combined with reinforced nonwoven was immersed in a gelation water bath. A reinforced membrane was subsequently formed.

### Membrane Performances

Membranes were tested in high-pressure testing cells. The operating pressure was 100 psig, and various salt solutions were used as the testing solution. Salt rejection was determined by using a dissolved solid meter. Furthermore, water flux was determined

by accumulating the volume of permeate material, which had flowed down from the cells.

## RESULTS AND DISCUSSION

### Effect of Membrane Preparing Conditions on Membrane Performances

#### Effect of SPSf/PSf Blending Ratios

The effects of SPSf/PSf blending ratios on the membrane performances are displayed in Table I. Water flux increased, and salt rejection decreased with an increase of SPSf/PSf blending ratios ranging from 1 : 9 to 1 : 2. This phenomenon was attributed to the fact that increasing the SPSf/PSf blending ratio (e.g., increasing the amount of hydrophilic SPSf in a fixed solid content) would lead to swelling of the membrane in water, thereby yielding a higher water flux. On the other hand, the swollen membrane in water led to the formation of larger channels, subsequently resulting in a lower salt rejection. Similar results were also obtained by Dinno et al.<sup>8</sup> The blending ratio of 1 : 3 was used in the following experiments because of its resulting appropriate combination of water flux with salt rejection.

Evaporation time sensitively affected the membrane performances during the preparation of SPSf/PSf blending membranes. Salt rejection of 0% was observed as the evaporation time was less than or equal to 120 sec. Therefore, an evaporation time of 180 sec was used to prepare the SPSf/PSf blending membranes without any additives.

#### Effect of THF

The effect of the content of THF on the membrane performances is displayed in Table II. Experimental data revealed that water flux decreased and salt re-

**Table I** Effects of SPSf/PSf Blending Ratios on the Performances of Membranes

SPSf/PSf Blending Ratios	SR (%)	WF (GFD)
2/1	12.0	42.8
1/1	22.9	27.5
1/2	25.0	21.4
1/3	30.0	15.9
1/5	29.5	10.6
1/9	26.0	10.1

Formulation: (SPSf/PSf)/NMP = 30/70%. Evaporation time: 180 sec.

**Table II** Effects of THF on the Performances of SPSf/PSf Blending Membranes

Content of THF (%)	Evaporation Time					
	5 sec		60 sec		180 sec	
	SR (%)	WF (GFD)	SR (%)	WF (GFD)	SR (%)	WF (GFD)
2.5	—	—	—	—	32.4	11.2
5.0	1.8	391.6	2.3	225.5	25.4	15.0
15.0	1.0	314.9	28.8	23.1	34.8	2.4
25.0	9.8	109.9	34.4	12.3	—	—
35.0	15.6	67.7	—	—	—	—

Formulation: (SPSf/PSf)/THF/NMP = 30/X/70 - X%.

jection increased with raising the content of THF, which is a volatile solvent. This could have occurred due to an increase of the content of THF, which would have accelerated the formation of smaller pores. Consequently, higher salt rejection and the lower water flux were observed. A comparison was also made of the difference between both SPSf/PSf blending membranes with or without an addition of THF. For those membranes with similar membrane performance, the evaporation time required to prepare the SPSf/PSf blending membranes with the addition of THF was less than that of those SPSf/PSf blending membranes without the addition of THF. This phenomenon could be accounted for by the fact that adding the volatile THF would accelerate the formation of a membrane barrier.

### Effect of Gelation Temperature

The effects of gelation temperature on membrane performances are listed in Table III. Water flux increased from 3.0 to 15.9 gfd, and salt rejection increased from 20.0 to 30.0% as gelation temperature dropped from 40 to 4°C. This occurrence was attributed to a smaller pore size and formation of a

**Table III** Effects of Gelation Temperature on Membrane Performances

Gelation Temp (°C)	SR (%)	WF (GFD)
4	30.0	15.9
10	26.4	16.6
25	26.8	16.5
40	20.0	3.0

Formulation: (SPSf/PSf)/NMP = (1/3)30/70%. Evaporation time: 180 sec.

higher porosity as those membranes gelled in a lower temperature water bath.

### Effect of APSf/PSf Ratios

The effect of the APSf/PSf blending ratios on membrane performances is displayed in Table IV. Incompatibility of the casting solution was observed for the APSf/PSf blending ratio of 1 : 2. Water flux displayed no appreciable difference between both membranes, which had the APSf/PSf blending ratios of 1 : 3 and 1 : 9, respectively. Salt rejection of the membrane with the APSf/PSf blending ratio of 1 : 3 was higher than that with the APSf/PSf blending ratio of 1 : 9. These results were different from those of the various SPSf/PSf blending ratios affecting membrane performances. This discrepancy was probably due to the fact that an increase in the amount of APSf would increase the charge density of a membrane, subsequently leading toward the rise in salt rejection. The swelling effects of both APSf/PSf blending membranes in water were similar, thereby leading to the almost equivalent water flux.

**Table IV** Effects of APSf/PSf Blending Ratios on Membrane Performances

APSF/PSf Blending Ratios	SR (%)	WF (GFD)
1 : 2	Uncombined	
1 : 3	37.7	6.9
1 : 9	23.2	6.8

Formulation: (APSF/PSf)/NMP = 30/70%. Evaporation time: 10 sec.

**Table V** Effects of Additives on the Performances of SPSf/PSf Blending Membranes

Additive	SR (%)	WF (GFD)
Non	0	—
Acetic acid	39.3	11.1
Maleic acid	30.0	8.9
Lactic acid	—	Low

Formulation: (SPSf/PSf)/Additive/NMP = (1/3)30/5/65%.  
Evaporation time: 60 sec.

### Effect of Additives

Membrane performances were affected as the additive was added into the casting solution of SPSf/PSf blending. As shown in Table V, the evaporation time of 60 sec was used for preparing the SPSf/PSf blending membrane involved with an additive of acetic acid or maleic acid. Unacceptably low water flux was observed when the evaporation time of 180 sec was used for preparing these membranes. This phenomenon was due to the fact that a membrane barrier would be formed in a shorter evaporation time as an additive was added into the casting solution of the SPSf/PSf blend.

The effects of these additives on the performance of APSf/PSf blending membranes are displayed in Tables VI and VII. Salt rejection and water flux dropped off as maleic acid or  $(\text{CH}_3\text{COO})_2\text{Mn}$  were added to the casting solution. Addition of one of these additives of THF,  $\text{ZnCl}_2$ ,  $\text{CuCl}_2$ , and acetic acid into the casting solution could increase water flux and decrease salt rejection of the membrane. Table VII shows the relationship between the content of acetic acid and the performances of these APSf/PSf blending membranes for two evaporation times. As the content of acetic acid increased from

**Table VI** Effects of Additives on Performances of APSf/PSf Blending Membranes

Additive	SR (%)	WF (GFD)
Non	37.7	6.9
THF	15.0	76.0
Maleic acid	28.1	4.6
$\text{ZnCl}_2$	27.0	29.3
$\text{CuCl}_2$	15.3	30.0
$(\text{CH}_3\text{COO})_2\text{Mn}$	24.7	3.0

Formulation: (APSF/PSF)/Additive/NMP = (1 : 3)30 : 5 : 65%.  
Evaporation time: 10 sec.

**Table VII** Effects of the Content of Acetic Acid on Performances of APSf/PSf Blending Membranes

Content of Acetic Acid (%)	Evaporation Time			
	10 sec		30 sec	
	SR (%)	WF (GFD)	SR (%)	WF (GFD)
0	37.7	6.9	—	—
2.5	16.6	65.6	18.8	51.9
5.0	16.7	64.0	30.0	24.9
10.0	22.4	61.0	40.1	15.9

Formulation: (APSF/PSF)/Acetic acid/NMP = (1/3)30/X/70 - X%.

2.5 to 10%, the growth rate of salt rejection and the declining rate of water flux of membranes with the evaporation time of 30 sec were faster than those with the evaporation time of 10 sec. This phenomenon was probably due to the fact that the higher content of acetic acid rapidly formed smaller pores at a longer evaporation time.

### Effect of Salt Testing Solutions on Membrane Performances

Table VIII summarizes the relationship between salt testing solutions and membrane performances for both SPSf/PSf and APSf/PSf blending membranes. The order of salt rejection was  $\text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{NaCl} > \text{MgCl}_2$  for SPSf/PSf blending membranes, and the order of salt rejection was  $\text{MgCl}_2 > \text{NaCl} > \text{MgSO}_4 > \text{Na}_2\text{SO}_4$  for the APSf/PSf blending membranes. These results could be accounted for by the fact that the salt rejection was affected by the different varieties of salts, which consisted of

**Table VIII** Effects of Salts on the Performances of Both SPSf/PSf and APSf/PSf Blending Membranes

Salts	Formulation/SR (%)	
	APSF/PSF/NMP	SPSF/PSF/NMP
Tap Water	31.4	23.3
NaCl	26.7	23.8
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	9.6	75.1
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	15.2	25.6
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	59.0	10.8

(APSF/PSF)/NMP = (1/3)30/70%; (SPSF/PSF)/NMP = (1/3)30/70%.

anion and cation for various valences and the charged character of membranes. The SPSf/PSf blending membranes were negatively charged membranes which would more effectively reject divalent anion and, conversely, less effectively reject divalent cation. This phenomenon is referred to as the Donnan Effect. A similar reason was also used to account for the result of APSf/PSf blending membranes rejecting the above-mentioned salts. A similar observation was also reported by Urairi et al.<sup>9</sup> and Huang and Kim.<sup>10</sup>

## SUMMARY

The SPSf/PSf and APSf/PSf blending membranes were successfully prepared in this study via the addition of hydrophilic and charged SPSf or APSf. Consequently, the membrane performances of original polysulfone were improved.

Water flux and salt rejection of both SPSf/PSf and APSf/PSf blending membranes were influenced by altering the polymer blending ratios, additives, evaporation time, and gelation temperature. The SPSf/PSf blending membranes involved no additives in which the membrane performances were sensitively influenced by evaporation time. For instance, the salt rejection of SPSf/PSf blending membranes was 0%, as the evaporation time was less than or equal to 120 sec. Increasing the SPSf/PSf blending ratio from 1 : 9 to 1 : 2 would increase the water flux as well as decrease the salt rejection.

The order of salt rejection for the SPSf/PSf blending membranes rejecting four varieties of salts was  $\text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{NaCl} > \text{MgCl}_2$ . Additionally, the opposite order was obtained by the APSf/PSf blending membranes.

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