

Fouling Reduction of a Poly(ether sulfone) Hollow-Fiber Membrane with a Hydrophilic Surfactant Prepared via Non-Solvent-Induced Phase Separation

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ABSTRACT: Membrane fouling is still a crucial problem, especially in applications for water treatment. When fouling takes place on membrane surfaces, it causes flux decline, leading to an increase in production cost due to increased energy demand. The selection of the right membrane material and a special treatment of the membrane are required to avoid membrane fouling. This article reports the fouling resistance of a poly(ether sulfone) (PES) hollow-fiber membrane modified with hydrophilic surfactant Tetronic 1307. Experiments on several methods of fouling were carried out to investigate the effect of the addition of nonionic surfactant Tetronic 1307 on membrane fouling. The effectiveness of a chemical agent [sodium hypochlorite (NaClO)] in the reduction of bovine serum albumin (BSA) deposition on the membrane surface

was also evaluated. Permeation results showed that the fouling of a PES blend membrane with Tetronic 1307 was lower than that of the original PES membrane in the case of BSA filtration. A treatment with a 100 ppm NaClO solution was capable of removing BSA cake formation and effective at improving the relative permeability. The permeability of a PES blend membrane with Tetronic 1307 was almost 2 times higher than the original permeability when the membrane was treated with a 100 ppm NaClO solution because both BSA and Tetronic 1307 could be decomposed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1653–1658, 2009

Key words: membrane fouling; phase separation; poly(ether sulfones)

INTRODUCTION

Ultrafiltration was developed for applications in separation processes. In recent years, this membrane technology has received attention as an attractive method for water treatment.^{1–4} Membrane manufacturers are developing high-performance membrane filters with high flux, high rejection, high mechanical stability, and good chemical resistance for useful applications in this emerging industry. Nowadays, poly(ether sulfone) (PES) ultrafiltration membranes are dominating the international membrane market because of their good ultrafiltration rating and high permeability.³ PES is well known for its excellent chemical resistance and good thermal stability and mechanical properties. This polymer is widely used in membrane preparation for various applications.^{4,5} However, the hydrophobic property of pure PES is the main disadvantage of this polymer because of fouling problems in practical applications. Generally, fouling can be defined as reversible and irreversible

deposition of a material onto or into the membrane causing loss of flux. Irreversible fouling is especially significant in applications for protein separation because hydrophobic interactions between proteins and the membrane surface bring about nonselective irreversible adsorption of proteins onto the membrane surface.^{6–10} Hydrophilic modification of the membrane surface is one of the methods of minimizing protein adsorption and preventing membrane fouling.^{10,11} Increasing the membrane surface hydrophilicity can effectively minimize protein adsorption and prevent membrane fouling.² Qiu et al.¹¹ reported the influence of the addition of Pluronic F127 on the structural formation of a poly(vinyl butyral) (PVB) hollow-fiber membrane prepared via thermally induced phase separation.¹ The contact angle of water of a Pluronic F127-PVB blend membrane was about 10° smaller than that of the original PVB membrane, and this indicated an increase in the hydrophilicity. Rahimpour and Madaeni⁴ succeeded in producing a PES hydrophilic membrane modified by cellulose acetate phthalate. The antifouling property of the flat PES membrane was improved by the addition of a small amount of cellulose acetate phthalate to the casting solution. Another method well known for controlling

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membrane fouling during applications is a chemical treatment. In practical applications, this method is required when the foulants are not removed by backwashing.¹² Chemical agents have been widely used for cleaning to optimize membrane performance and minimize operation costs. This method is especially useful for solving the problem of irreversible fouling that is not removed by a normal backwash procedure. Various experiments have been conducted to improve our understanding of the effect of this chemical cleaning on the membrane performance.^{8,13,14}

In our previous study,¹⁵ a PES hollow-fiber membrane was successfully modified by the addition of a surfactant additive (Tetronic 1307) to improve the membrane performance. The contact angles of water on the membrane outer surface decreased with the addition of Tetronic 1307, and this indicated that the membrane became more hydrophilic. The addition of Tetronic 1307 was useful for improving the water permeability and obtaining a hydrophilic membrane surface. In this work, we studied the effect of the addition of Tetronic 1307 on the fouling property of the membrane. The effect of a chemical agent [sodium hypochlorite (NaClO)] on the permeability of PES hollow-fiber membranes was also investigated.

EXPERIMENTAL

Materials

PES (E6020; weight-average molecular weight = 65,000) and surfactant Tetronic 1307 (weight-average molecular weight = 18,000, hydrophile-lipophile-balance (HLB) > 24) were purchased from BASF Co. (Ludwigshafen, Germany). *N*-Methyl-2-pyrrolidone, bovine serum albumin (BSA; Cohn Fraction V), and NaClO (chlorine content = 5%) were purchased from Wako Pure Chemical Industries, Co., Ltd. (Osaka, Japan). All the chemicals were used without further purification.

Preparation of the hollow-fiber membrane

The hollow-fiber membrane was prepared via non-solvent-induced phase separation by a batch extruder as previously described.¹⁵ Dope solutions were prepared through the dissolution of PES and Tetronic 1307 in *N*-methyl-2-pyrrolidone by stirring for 24 h at room temperature. Two dope composition types for the original PES and blend membranes were prepared. The concentrations of PES were 22 and 25 wt % for the original and blend PES membranes, respectively. Moreover, 7 wt % Tetronic 1307 was added to the dope for the blend membrane. The polymer concentrations were changed in both cases because the same initial water permeabilities for

TABLE I
Conditions of Membrane Preparation

Polymer flow rate (m/min)	3.20
Internal coagulant flow rate (m/min)	10.4
Take-up speed (m/min)	11.2
Internal coagulant	Water
External coagulant	Water
Air-gap distance (cm)	5
External coagulant temperature (°C)	20
Dope temperature (°C)	20
Internal coagulant temperature (°C)	20

both membranes could be achieved. The homogeneous dope solutions were left in the reservoir for 4–7 h to allow the complete release of bubbles. The conditions of membrane preparation were set up to be constant for both cases, as tabulated in Table I. The prepared hollow-fiber membranes were kept in the pure water before testing.

Investigation of the fouling property

The laboratory-scale apparatus used for the analysis of the fouling property of the PES membrane was set up at room temperature ($25 \pm 1^\circ\text{C}$). A detailed description is provided in a previous work.¹⁶ A filtration solution was forced to permeate from the inside to the outside of the hollow-fiber membrane. The transmembrane pressure was applied by the adjustment of the pressure valve close to the release side, and the average of the readings of the two pressure gauges (ranging from 0.05 to 0.1 MPa) was taken as the feed pressure. BSA solutions with a concentration of 1000 ppm were prepared for membrane fouling experiments. The pH of the solutions was adjusted to 7.0 ± 1 with sodium dihydrogen phosphate.

Three series of fouling experiments were carried out over a period of 11 h in three filtration steps. In the first series of experiments, filtration was conducted with deionized water in the first step of filtration (1 h). BSA solutions were used as feed solutions in the second step of filtration. After 3 h of BSA filtration, each feed solution was subsequently changed with deionized water in the third step for 7 h of filtration. The second and third series of fouling experiments were conducted with the same first and second steps of filtration used in the first series of experiments. However, NaClO solutions of 10 and 100 ppm were used as feed solutions in the third step of filtration for the second and third series of experiments, respectively. Permeability through the hollow-fiber membrane was determined by the collection and weighing of permeates every 5 min until the end of filtration. The permeability was calculated on the basis of the inner surface area of the hollow-fiber membrane.

For rejection testing, a solution of 1 wt % dextran with an average molecular weight of 10,000 was

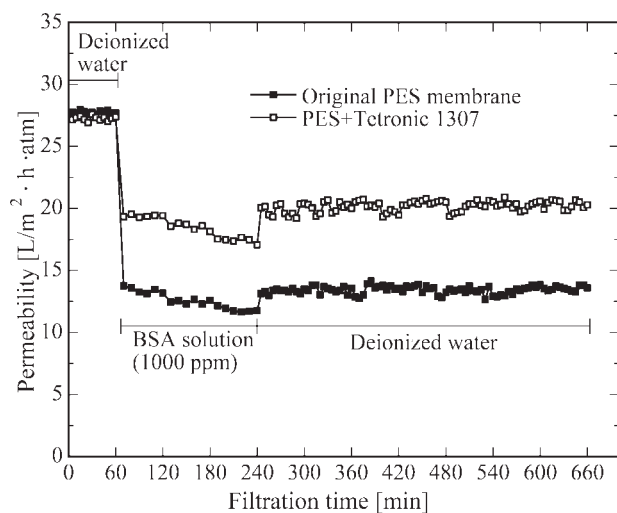


Figure 1 Time course of water permeability of the PES hollow-fiber membrane. The final feed solution was deionized water.

used as the feed solution. The filtration procedure was the same as that used in the water permeability experiment. Rejection of the hollow-fiber membrane was calculated by the measurement of the refraction indices of the feed and permeate solutions.¹⁵

RESULTS AND DISCUSSION

Membrane flux and fouling phenomena

As described previously, PES hollow-fiber membranes with and without Tetronic 1307 were prepared via a non-solvent-induced separation method with different polymer concentrations to obtain the same initial value of membrane flux. This study was focused on the effect of the addition of Tetronic 1307 on the membrane fouling property. The results are presented as the time course of the membrane permeability.

Figure 1 shows the results of the first series of fouling investigations. The permeabilities of the two membranes were almost the same at the beginning of deionized water filtration. When the BSA solution was fed as a filtration solution, the flux of the original PES membrane suddenly decreased to about 50% of the initial permeability. Under the same conditions, the permeability of the PES blend membrane with 7 wt % Tetronic 1307 was 2 times higher than that of the original PES membrane. The permeability reduction of the original PES membrane with the initial filtration of the BSA solution was attributed to adsorption or deposition of protein molecules on the pore surface of the membrane. Some BSA molecules adsorbed onto the surface could actively contribute to the formation of the cake layer.^{17,18} The water contact angles of the original PES membrane and the PES blend membrane with Tetronic 1307 were 75 and 63°, respectively.¹⁵ The existence of a poly(ethyl-

ene oxide) (PEO) segment in Tetronic 1307 was attributed to increased hydrophilicity of the blend membrane, which resulted in reduced protein adsorption in this system. Thus, the low fouling property of the PES blend membranes was attributed to the hydrophilicity properties of the PEO segment contained in Tetronic 1307. The forces of the interaction between the membrane surface and solutes are important in understanding fouling phenomena. Jeon et al.^{17,18} studied PEO surface-protein interactions. On the basis of their experiments, they proposed that the protein approaching the PEO surface initiates the compression of PEO chains, which induces steric repulsion; as a result, the adsorption of the protein is unlikely to occur. Thus, a PEO chain on the surface of the blend membrane may repress membrane fouling.

After 3 h for BSA filtration, deionized water was subsequently fed into the hollow-fiber membrane. Under this condition, the permeability of the original PES membrane was increased from 11.8 to 13.5 L/m² h atm. On the other hand, the permeability of the PES blend membrane increased from 17.1 to 20.1 L/m² h atm. The difference in the permeability recovery between these two membranes may be related to protein desorption on the membrane surface. Because the protein was likely to desorb from the hydrophilic surface, the permeability was recovered more in the blend membrane.

Effect of the NaClO treatment on the membrane fouling

To investigate the effect of a chemical agent on the fouling phenomena of PES hollow-fiber membranes,

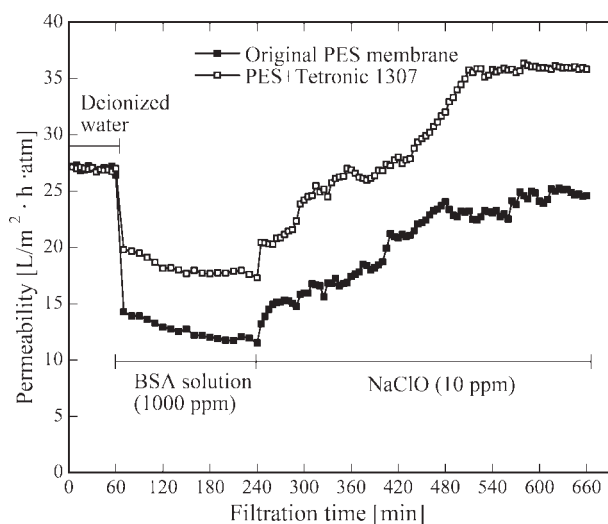


Figure 2 Time course of water permeability of the PES hollow-fiber membrane. The final feed solution was a 10 ppm NaClO solution.

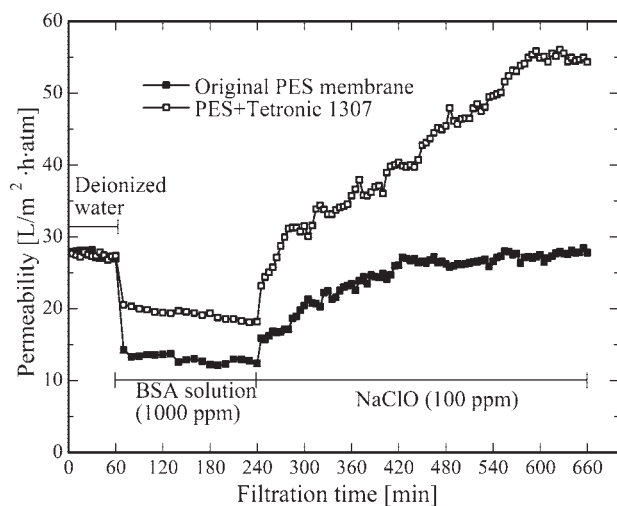


Figure 3 Time course of water permeability of the PES hollow-fiber membrane. The final feed solution was a 100 ppm NaClO solution.

aqueous NaClO solutions were used as feed solutions. Figure 2 shows the fouling tendency of the PES hollow-fiber membrane when an aqueous NaClO solution with 10 ppm was used in the third step of filtration. At the end of BSA filtration, the permeabilities were 11.5 and 17.3 L/m² h atm for the original PES and PES blend membranes, respectively. When the filtration experiment was continued with an NaClO solution, the permeabilities increased and reached the maximum after about 6 h of filtration. The maximum permeabilities were 24.8 and 35.9 L/m² h atm for the original PES and PES blend membranes, respectively. The maximum permeability of the PES blend membrane was higher than that of the original PES membrane. Some parts of BSA deposited onto the membrane surface could be decomposed and removed with a hypochlorite solution. Thus, the permeabilities for both membranes increased after the filtration of the NaClO solution. Moreover, when the membrane was brought into contact with a hypochlorite solution, some parts of Tetronic 1307 decomposed and eventually leached from the membrane, and this led to the porous structure.¹⁹ Therefore, the permeability of the blend membrane with Tetronic 1307 was enhanced greatly, and the final permeability actually reached a value higher than the initial permeability.

The fouling and recovery properties usually depend on features of the pore structure, such as the pore size and porosity. In our previous study,¹⁹ we measured the surface structure after an NaClO treatment with atomic force microscopy measurements. The NaClO treatment brought about a reduction of the nodule size on the outer surface. However, the changes in the pore size and porosity were not so pronounced.

In the third series of fouling experiments, an aqueous hypochlorite solution (100 ppm) was used as a

feed solution after 3 h of BSA filtration. The time course of the water permeability is shown in Figure 3. As shown in Figure 3, when the aqueous NaClO solution was filtered, the permeability of the original PES membrane gradually increased and reached a maximum of 27.6 L/m² h atm after 3 h of filtration. On the other hand, the permeability of the PES blend membrane sharply increased and reached a maximum of 54.9 L/m² h atm after 6 h of filtration. The maximum permeability of the PES blend membrane was about 2 times higher than that of the original PES membrane.

To analyze the permeability tendency of the fouled membrane treated with NaClO, we calculated the permeability recovery ratio, which is defined as $(J_1 - J_2)/J_0$. Here, J_0 , J_1 , and J_2 represent the initial permeability of the membrane at the beginning of water filtration, the constant membrane permeability at the end of filtration after 11 h, and the membrane permeability just after the BSA filtration, respectively. The results of this calculation are presented in Figure 4. In general, the permeability recovery ratio increased with the addition of NaClO for both the original PES and PES blend membranes. In all cases, the PES blend membrane showed better performance. In the case of deionized water, because BSA was likely to desorb from the hydrophilic surface, the PES blend membrane showed a higher permeability recovery ratio. When the NaClO solutions were used, Tetronic 1307 could also be decomposed by NaClO and BSA deposited on the membrane, and so a higher permeability recovery ratio was obtained.

Relative permeabilities of membranes treated with NaClO solutions

Two NaClO treatment methods were used to investigate the effect of the treatments on the relative permeability of virgin and fouled membranes. In the

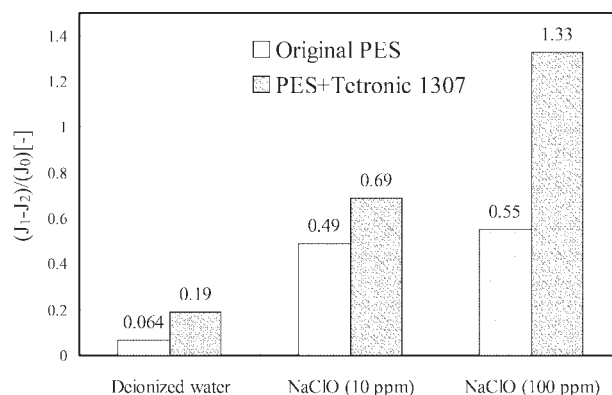


Figure 4 Permeability recovery ratio of fouled membranes treated with deionized water or 10 or 100 ppm NaClO solutions.

first method, the hollow-fiber membrane was immersed in an NaClO solution as previously described.¹⁹ Virgin membranes of both the original PES and PES with Tetronic 1307 were immersed in 10 or 100 ppm NaClO. After 3 h of immersion, the membranes were kept in deionized water for 24 h, and subsequently, their water permeability was checked. This permeability was defined as J_3 . The values of J_3/J_0 were compared with the relative permeability (J_1/J_0) of the fouled membrane treated with another method. As described previously, these treatments involved the NaClO solution flowing inside the fouled hollow-fiber membrane. The results are summarized in Table II. In the case of deionized water, J_3 was equal to J_0 , and J_3/J_0 was unity for both the original PES membrane and PES blend membrane. J_1/J_0 became 0.48 for the original PES membrane and 0.75 for the PES blend membrane. Thus, the PES blend membrane had better performance in the case of water treatment, as described previously.

When the original PES membrane was immersed in aqueous NaClO solutions of 10 or 100 ppm, J_3 was hardly changed because PES could not be decomposed by NaClO.¹⁹ Thus, the value of J_3/J_0 was almost equal to unity. The relative permeabilities of the original PES membrane were 0.91 and 0.98 when NaClO concentrations were 10 and 100 ppm. Therefore, the relative permeabilities were close to the values of J_3/J_0 . This indicated that these treatments in which an NaClO solution flowed inside the fouled hollow-fiber membrane were useful for decomposing BSA deposited on or inside the membrane.

On the other hand, because Tetronic 1307 within the PES blend membrane could be decomposed by NaClO,¹⁹ the value of J_3/J_0 increased to 1.5 and 2.0 with 10 and 100 ppm NaClO solution treatments, respectively. Also in this case, J_1/J_0 was close to the value of J_3/J_0 . This occurred because not only BSA but also Tetronic 1307 could be decomposed by NaClO. The relative permeability reached about 2 in the case of the 100 ppm NaClO treatment.

To investigate the effect of the NaClO treatment on the solute rejection, some solute rejection experiments were carried out. The results are shown in Table III. The solute rejection of the PES blend mem-

TABLE III
Rejection Performance of the PES Hollow-Fiber Membrane Before and After Its Treatment with a Hypochlorite Solution (100 ppm)

Membrane sample	Rejection of dextran (%) ^a
PES	92.9
PES (treated with NaClO)	92.9
PES/Tetronic 1307 (7 wt %)	85.7
PES/Tetronic 1307 (7 wt %); treated with NaClO)	82.2

^a Weight-average molecular weight = 10,000.

brane [Tetronic 1307 (7 wt %)] was lower than that of the original PES membrane. However, the hypochlorite treatment (100 ppm) hardly had a significant impact on the rejection performances of the PES blend membrane or the original PES membrane. On the basis of this rejection result, we have concluded that the hypochlorite treatment of the PES hollow-fiber membrane in this work does not cause the deterioration of the molecular weight cutoff performance of the membrane.

CONCLUSIONS

The effect of the addition of hydrophilic surfactant Tetronic 1307 on the fouling property of PES membranes was investigated. The permeability decline of the PES blend membrane with Tetronic 1307 in BSA filtration was lower than that of the original PES membrane because of its greater hydrophilicity. When water flowed inside the fouled hollow-fiber membrane after BSA filtration, the permeability was recovered. The permeability recovery of the PES blend membrane was higher than that of the original PES membrane. This indicated that the addition of Tetronic 1307 to the preparation of the membrane was very useful for the desorption of BSA deposited on the membrane. When membranes were treated with NaClO solutions, the permeabilities of the fouled membranes were significantly recovered. The PES blend membrane showed better performance than the original PES membrane because both BSA and Tetronic 1307 could be decomposed by NaClO.

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TABLE II
Relative Permeabilities of the PES Membrane Treated with Deionized Water and Aqueous NaClO Solutions

Solution	Original PES membrane		PES blend membrane	
	J_3/J_0	J_1/J_0	J_3/J_0	J_1/J_0
Deionized water	1.0	0.48	1.0	0.75
10 ppm NaClO solution	1.0	0.91	1.5	1.32
100 ppm NaClO solution	1.0	0.97	2.0	1.98

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