

Effect of the Addition of the Surfactant Tetronic 1307 on Poly(ether sulfone) Porous Hollow-Fiber Membrane Formation

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ABSTRACT: Poly(ether sulfone) (PES) hollow-fiber membrane was prepared via a nonsolvent-induced phase-separation method, and the effect of the addition of the surfactant Tetronic 1307 on the membrane performance and characteristics was investigated. The phase diagram of the PES/*N*-methyl-2-pyrrolidone (NMP)/water system was clarified. When the polymer solution involved Tetronic 1307, the amount of water required to induce the phase separation decreased, which indicated that Tetronic 1307 was one kind of nonsolvent. The kinetics of phase separation for the PES/NMP/Tetronic 1307 system were studied by light-scattering measurements. With the addition of Tetronic 1307, delayed phase separation was observed, and the structure growth rate decreased. Scanning electron microscopy images for all of the membranes showed the formation of fingerlike macrovoids through the cross section. Membrane surface morphologies were measured by atomic force microscopy. The

obtained results indicated that membrane with 7 wt % Tetronic 1307 had higher roughness parameters than original membrane without the addition of surfactant. Ultrafiltration experiment results showed that the addition of Tetronic 1307 brought about an increase in water permeability and decreased the rejection of dextran with a molecular weight of about 10,000. The contact angles of water on the membrane outer surface decreased with the addition of Tetronic 1307. This means the membrane surface became more hydrophilic. Thus, the addition of Tetronic 1307 was useful for improving the water permeability and for obtaining a hydrophilic membrane surface. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3411–3418, 2008

Key words: membranes; poly(ether sulfones); nonsolvent induced phase separation; tetronic 1307; atomic force microscope; light scattering

INTRODUCTION

Porous polymeric membranes can be prepared several ways. The nonsolvent-induced phase-separation (NIPS) or immersion precipitation method is one of the major phase-separation methods that is mostly used to produce commercial porous polymeric membranes.^{1–6} In the membrane preparation process via NIPS, a polymer is dissolved in the solvent, and the homogeneous polymer solution is cast on a support or is extruded through a spinneret and subsequently immersed in a nonsolvent coagulant bath. Phase separation occurs because of the inflow of nonsolvent to the solution.^{1,2}

The addition of a third component to a casting solution has been one important technique in membrane preparation. Organics and inorganics added to the casting solution have been reported as pore-forming agents and membrane-modifying agents.^{7–13} Kim and Lee⁷ reported the influence of the addition of poly(ethylene glycol) (PEG) on the structure for-

mation of polysulfone flat membranes and permeation properties. With an increase in the amount of PEG additive, or the molecular weight of the PEG additive, the pore size of the surface became larger, and the top layer became more porous. Wang and coworkers^{9,10,12} succeeded in making a hydrophilic poly(ether sulfone) (PES) flat membrane by blending the surfactant Pluronic F127. Total membrane fouling and irreversible membrane fouling decreased with increasing Pluronic F127 content.

In this study, we used the surfactant Tetronic 1307 (weight-average molecular weight = 18,000) as a third component in the PES membrane formation to produce high hydrophilicity in the membrane surface. Tetronic, also available commercially as Poloxamine, is a tetrafunctional block polymer nonionic surfactant with four polyoxyethylene–polyoxypropylene blocks joined together by a central ethylenediamine bridge.¹⁴ In this study, PES hollow-fiber membranes were prepared via the NIPS process. The effect of the addition of the surfactant Tetronic 1307 on the performance of the final PES hollow-fiber membrane was investigated. Very few studies have been reported about the structure growth rate and pore formation from the polymer blending system via NIPS. However, knowledge of this pore forma-

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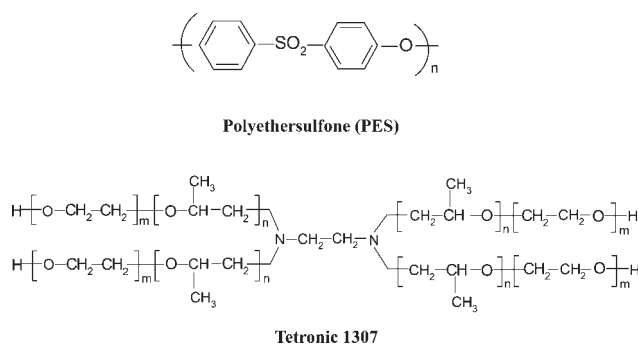


Figure 1 Chemical formulas of PES and Tetronic 1307.

tion is important for controlling the pore size of hollow-fiber membranes. Light-scattering experiments were done to obtain information on the structure growth rate. As far as we know, this is the first study in which blend PES/*N*-methyl-2-pyrrolidone (NMP)/Tetronic 1307 hollow-fiber membranes were prepared by the NIPS procedure.

EXPERIMENTAL

Material

PES (Ultrason E6020 P), with a weight-average molecular weight of 65,000, was purchased from BASF Co. (Ludwigshafen, Germany) NMP was obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Surfactant Tetronic 1307, with a molecular weight of 18,000 and a PEO content of 70 wt %, was purchased from BASF Co. Dextran, with an average molecular weight of 8500–11,500, was purchased from Sigma (Steinheim, Germany). All of the chemicals were used without further purification. The structures of PES and Tetronic 1307 are shown in Figure 1.

Cloud-point experiment

The determination of cloud point for the PES/NMP/water system was measured by a method similar to that described by Matsuyama et al.⁴ Homogeneous polymer solution samples were prepared by the dissolution of PES in the solvent NMP. Solutions with four different PES concentrations (10, 15, 20, and 25 wt %) were prepared. A small amount of nonsolvent was then successively added to each solution at a

temperature of 25°C. The light transmittances of the solutions were measured by a spectrophotometer (Hitachi U-2000, Tokyo, Japan) at a 500-nm wavelength. We determined the cloud point by noting the appearance of turbidity. The effect of Tetronic 1307 content on the cloud point was also measured by the same method.

Light-scattering measurement

Membrane formation by immersion precipitation was studied by the light-scattering method. The light-scattering measurements were carried out to obtain the structure growth data with a polymer dynamics analyzer (Otsuka Electronics Co., Osaka, Japan, DYNA-3000). The polymer solution was cast onto a glass plate with an applicator 254 μm thick. The cast solution with the glass plate was immediately immersed in a coagulation bath with a mixture of NMP and water (weight ratio of NMP to water = 80 : 20) located between the laser and the detector. The temperature of the nonsolvent was about 25°C. The structure growth behavior during the phase-separation process was monitored at time intervals of 0.3 s.

Hollow-fiber membrane preparation

The hollow-fiber membranes were prepared via NIPS by a batch extruder. The conditions for membrane preparation were set up to be constant for all cases. The conditions are summarized in Table I. Dope solutions were prepared by the dissolution of PES and Tetronic 1307 in NMP. PES concentration was fixed at 25 wt % and Tetronic 1307 concentrations were varied at 1, 3, 5, 7, and 10 wt %. The dope solutions were left in the reservoir for 4 h to allow complete release of bubbles. The hollow fiber was extruded from the spinneret and wound on a take-up winder after it entered the coagulation bath to induce phase separation and solidify the membrane. The spinneret consisted of outer and inner tubes, and their diameters were 1.00 and 0.70 mm, respectively. The polymer flow rate through to the spinneret was controlled by a gear pump. Water flowed on a trough into the inner tube to make a lumen of the hollow fiber. The prepared hollow-fiber membranes were kept in pure water before testing.

TABLE I
Hollow-Fiber Membrane Preparation Conditions

Polymer flow rate (m/min)	Water flow rate (m/min)	Take-up speed (m/min)	Air-gap distance (cm)	Temperature (°C)			
				Coagulation bath	Dope reservoir	Water injection	Collecting bath
3.20	10.4	11.2	5	20	20	20	20

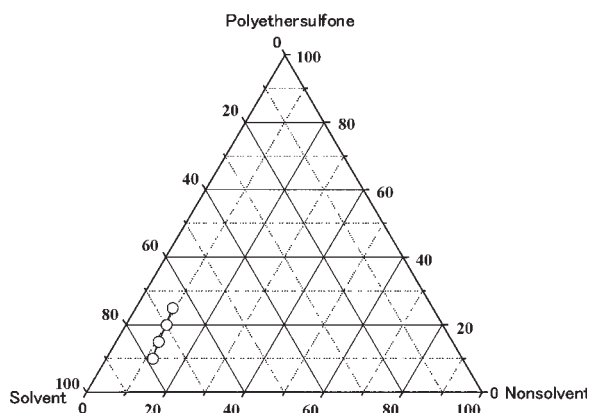


Figure 2 Phase diagram of the PES/NMP/water system (temperature = 25°C).

Characterization of the hollow-fiber membranes

We observed the hydrophilicity properties of the hollow-fiber membranes by measuring the water contact angle of the outer surface of the membrane at room temperature by a contact angle meter (Kyowa Kaiwenkagaku, Saitama, Japan, CA-A). Each contact angle was measured 20 times, and an average value was calculated. The membrane surface morphologies were measured with atomic force microscopy (AFM; SII NanoTechnology, Inc., Tokyo, Japan, SPA400). The AFM study techniques were given elsewhere.^{15–18} In this study, the hollow-fiber membrane sample was dried for 3 h with a freeze dryer (Eyela, FD-1000, Tokyo, Japan). The membrane outer surfaces were imaged in a scan area of 1 μm \times 1 μm . After 12 measurements, the average mean roughness was obtained from the AFM images.

The membrane morphologies (surface and cross section) were observed with scanning electron microscopy (SEM; Hitachi Co, S-800) with an accelerating voltage of 20 kV. For the cross-section observation, the freeze-dried hollow-fiber membranes were fractured in liquid nitrogen.

Water permeability through the hollow-fiber membrane was measured by a method similar to that described by Saito et al.¹⁹ Pure water was forced to permeate from the inside to the outside of the hollow-fiber membrane. The transmembrane pressure could be applied by 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. The water permeability was calculated on the basis of the inner surface area of the hollow-fiber membrane.

The solute rejection experiment was performed with the same apparatus as that used in the water permeability test. The solution that contained 1 wt % dextran with an average molecular weight of 8500–11,500 was used for the filtration test. Solute rejection of the membrane was obtained by measurement

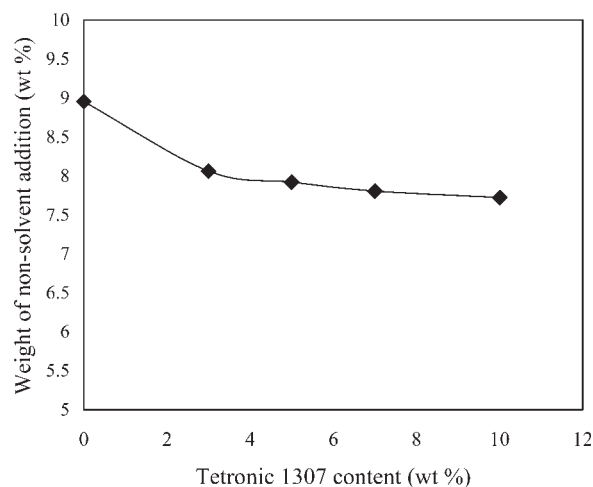


Figure 3 Relation between the amount of water required for the phase separation and the Tetronic 1307 content (initial PES concentration = 25 wt %).

of the refractive index of pure water, the feed dextran solution, and the permeate dextran solution by a refraction index measurement apparatus (Atago, Tokyo, Japan, model 3). The rejection of the hollow-fiber membrane (R) was calculated with eq. (1):

$$R = 1 - \left(\frac{n_J - n_W}{n_D - n_W} \right) \times 100\% \quad (1)$$

where n_J , n_D , and n_W represent the refraction indices of the permeate dextran solution, feed dextran solution, and pure water, respectively.

Retention ratios of Tetronic 1307 in the hollow-fiber membrane were measured by elemental analysis (Sumigraph NCH-21, Sumika Analysis Center Co., Japan). On the basis of the measured ratio of hydrogen to carbon, the retention ratios were calculated.

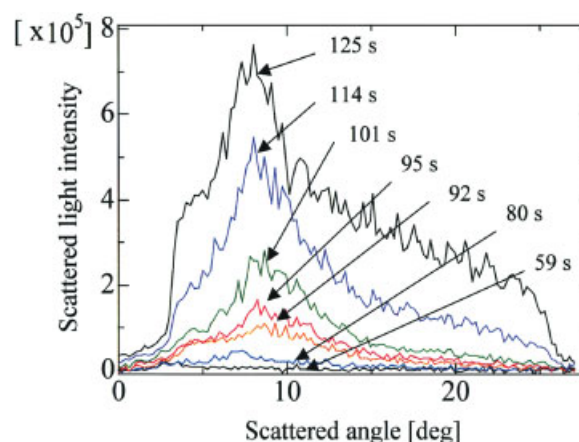


Figure 4 Light-scattering profiles (polymer concentration = 25 wt %, Tetronic 1307 concentration = 7 wt %, weight ratio of NMP to water in a nonsolvent bath = 80 : 20). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

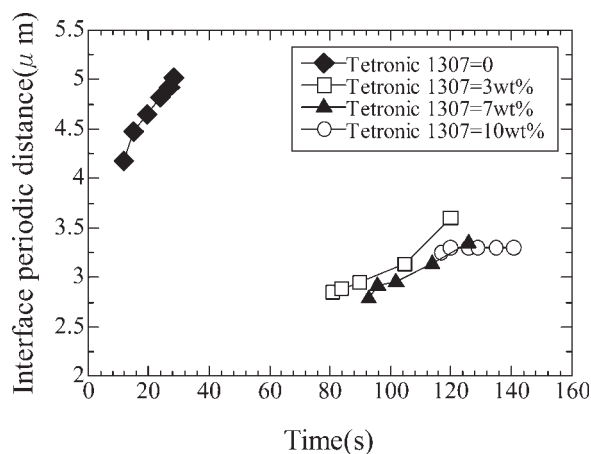


Figure 5 Time courses of the average interphase periodic distance.

RESULTS AND DISCUSSION

Cloud point

A phase diagram of the PES/NMP/water system is shown in Figure 2. The corners represent the pure components, and the axes represent the weight percentages. The cloud points were close to the PES–NMP axis, which indicated that even the addition of a small amount of nonsolvent (water) brought about phase separation in this system. For example, when the polymer weight percentage was 25%, the water

amount necessary for the phase separation was about 9%.

The effect of the addition of the surfactant Tetronic 1307 into the polymer solution on the cloud point is shown in Figure 3. The initial polymer weight fraction was fixed at 25 wt %; the amount of Tetronic 1307 varied. For all cases, the amounts of water required for phase separation are plotted in this figure. In the cases without Tetronic 1307, about 9 wt % water was necessary to induce phase separation. The amounts of water required to induce phase separation decreased when the addition of Tetronic 1307 increased. This indicated that Tetronic 1307 was one kind of nonsolvent, and a smaller amount of additional nonsolvent was necessary for phase separation with the increasing addition of Tetronic 1307.

Kinetic study

The kinetics of phase separation for the PES/NMP/Tetronic 1307 system was studied by light-scattering measurements. The light-scattering results obtained for the PES/NMP/Tetronic 1307 (7 wt %) system are shown in Figure 4. Similar patterns of light-scattering curves in the PES/NMP, PES/NMP/Tetronic 1307 (3 wt %), and PES/NMP/Tetronic 1307 (10 wt %) systems were also obtained, even though they are not shown here. In all systems, the scattered intensity (I_s) showed a maximum in the plot of I_s against the scattered angle (θ), which indicated that the

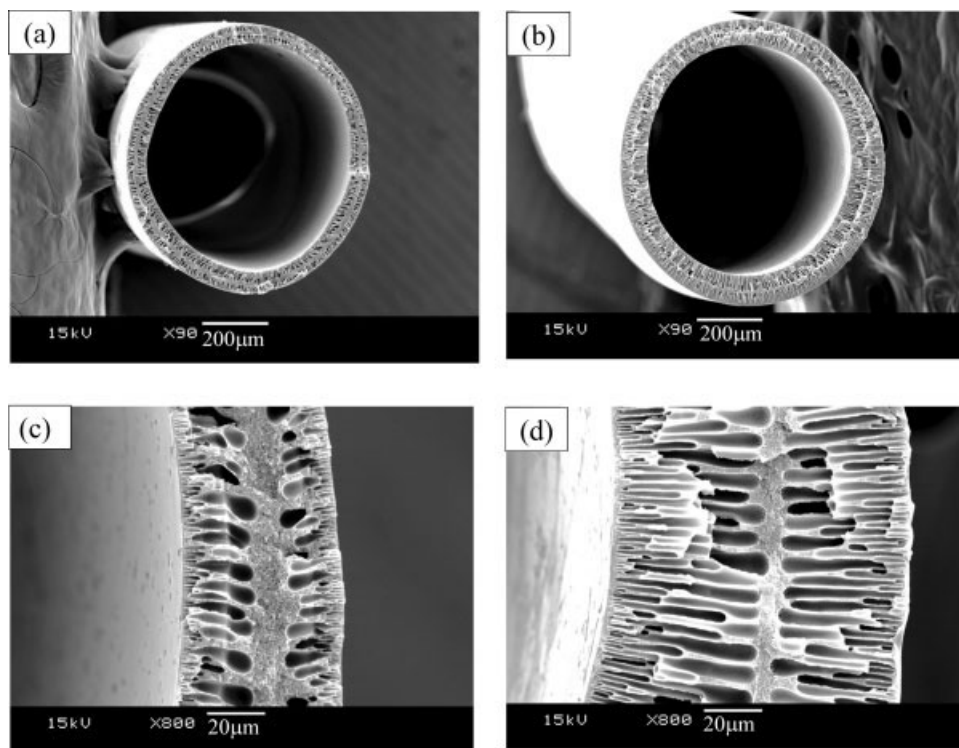


Figure 6 SEM images of whole cross sections and enlarged cross sections of PES hollow-fiber membranes: (a,c) without Tetronic 1307 and (b,d) with Tetronic 1307 (7 wt %).

phase separation occurred by spinodal decomposition.^{4,20,21} The location of the maximum intensity was shifted to the lower θ region with time. This shift of the peak position into the smaller angle region indicated the growth of the phase-separated structure.

The average interphase periodic distance (Λ) can be related to the θ at which I_s shows a maximum with eq. (2):

$$\Lambda = \frac{\lambda_0}{2n_0 \sin\left(\frac{\theta}{2}\right)} \quad (2)$$

where n_0 is the refractive index of the solution and λ_0 is the wavelength *in vacuo* (633 nm). Figure 5 shows the time course of Λ when the Tetronic 1307 content in the solution was changed. The abscissa denotes the time after the cast polymer solution was immersed in the nonsolvent bath. When Tetronic 1307 was not added to the polymer solution, phase separation occurred immediately, and the Λ growth rate of was fastest. On the other hand, delayed phase separation was observed with the addition of Tetronic 1307. The Λ growth rate also decreased. The molecular weight of Tetronic 1307 was 18,000, and thus, this surfactant is one kind of polymer. Therefore, with the addition of Tetronic 1307, the solution viscosity became higher. This led to the suppression of nonsolvent inflow to the polymer solution, which resulted in delayed phase separation. In addition, the higher solution viscosity brought about the lower growth rate of the phase-separated structure.

Membrane structures

The SEM images of whole cross sections and enlarged cross sections are shown in Figure 6 for both the original membrane prepared by the PES/NMP system and the membrane prepared by the PES/NMP/Tetronic 1307 (7 wt %) system. In both membranes, fingerlike macrovoids were clearly formed inside the hollow-fiber membranes.

Figure 7 show the cross-section structures near the inner and outer surfaces for various membranes. The number and length of macrovoids first increased with increasing Tetronic 1307 content in the polymer solution. As shown in Figure 3, the addition of Tetronic 1307 brought about the decrease in the nonsolvent amount necessary for phase separation, which meant the phase separation was likely to occur by the addition of Tetronic 1307. This may have been the reason for the enhanced growth of the macrovoid. However, further addition of Tetronic 1307 led to the formation of a sponge layer near the inner and outer surfaces, as shown in Figure 7(d). The increase in the polymer solution viscosity brought about by the addition of a large amount of Tetronic 1307 resulted in delayed phase separation. This

delayed phase separation is clearly shown in the light-scattering results in Figure 5. Usually, instantaneous phase separation leads to macrovoid formation, whereas delayed phase separation leads to the sponge structure.¹ Delayed phase separation in the case of the 10 wt % addition of Tetronic 1307 brought about the spongelike structure formation near the surface.

Figure 8 shows the inner and outer surface structures for both membranes with and without Tetronic 1307. The difference between the two membrane structures was not so clear because the pores were too small to be detected by SEM measurement. Therefore, a detailed investigation into the surface structure was done by AFM measurement.

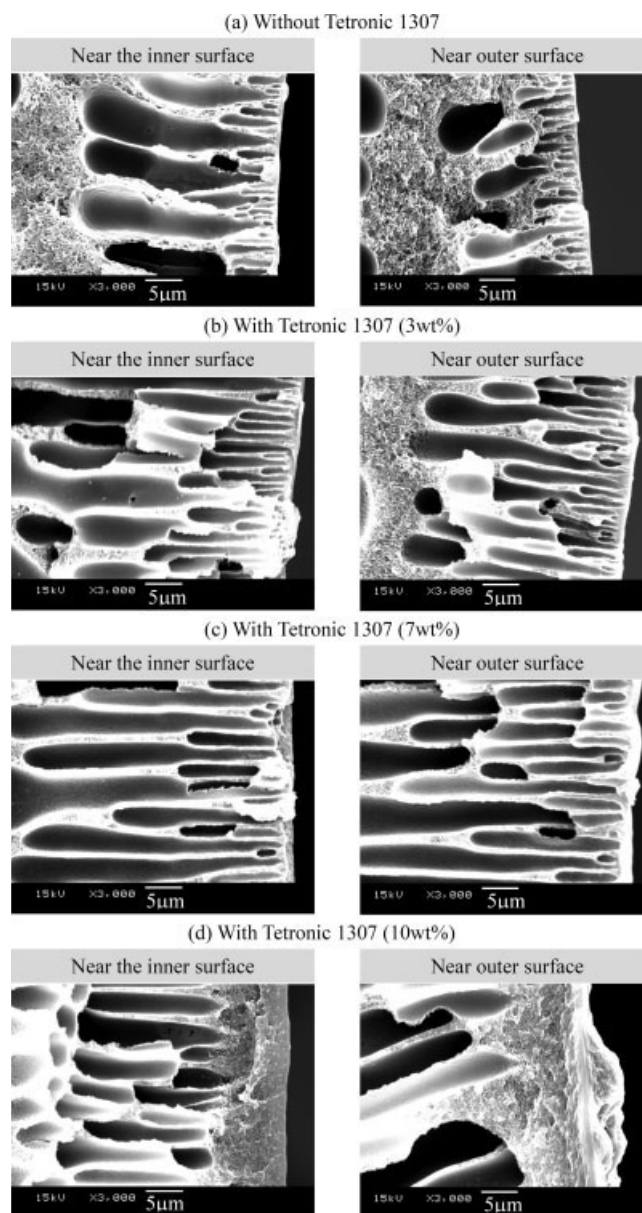


Figure 7 SEM images of the PES hollow-fiber membranes near both the inner and outer surfaces.

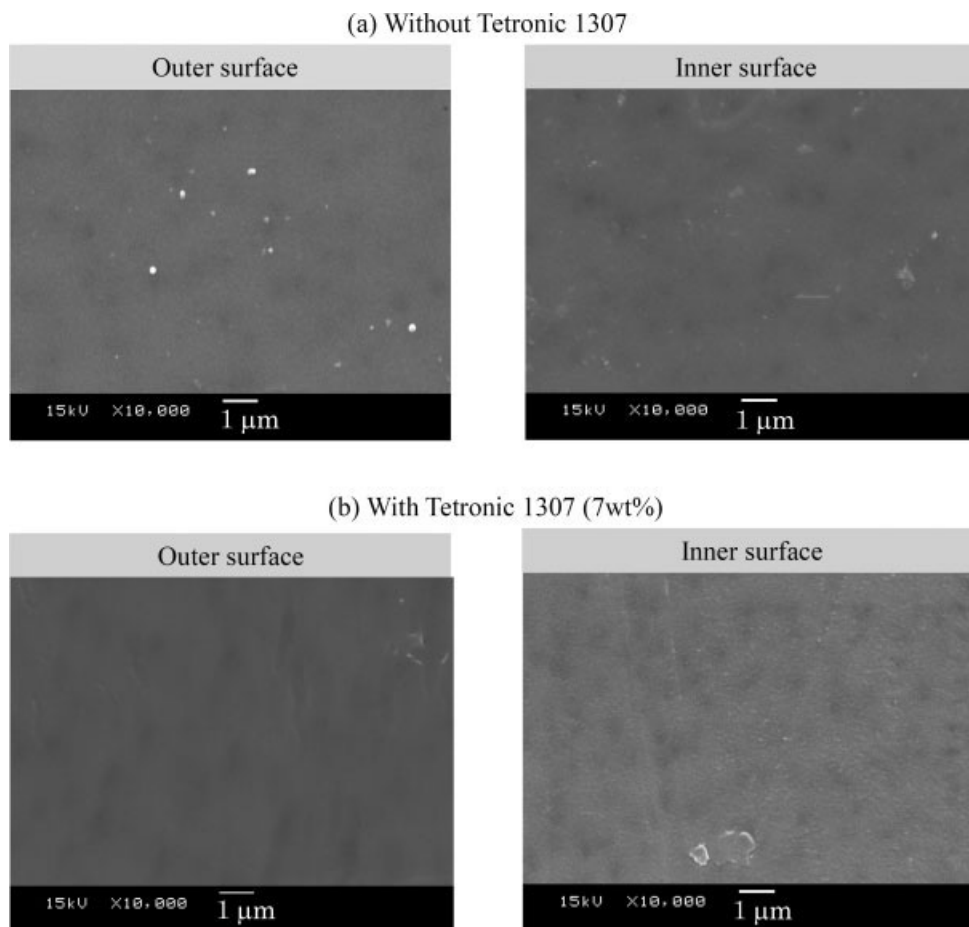


Figure 8 SEM images of the PES hollow-fiber membrane surfaces.

Figure 9 shows the AFM image of the outer surface for both membranes with and without Tetronic 1307. Clear nodular structures were observed, which are typical structures for ultrafiltration (UF) membranes.^{22,23} The mean roughnesses of the membranes

with and without Tetronic 1307 were 2.30 and 1.58 nm, respectively. The addition of Tetronic 1307 brought about an increase in the surface roughness. The existence of Tetronic 1307 at the surface may have attributed to this increase in roughness. However, further

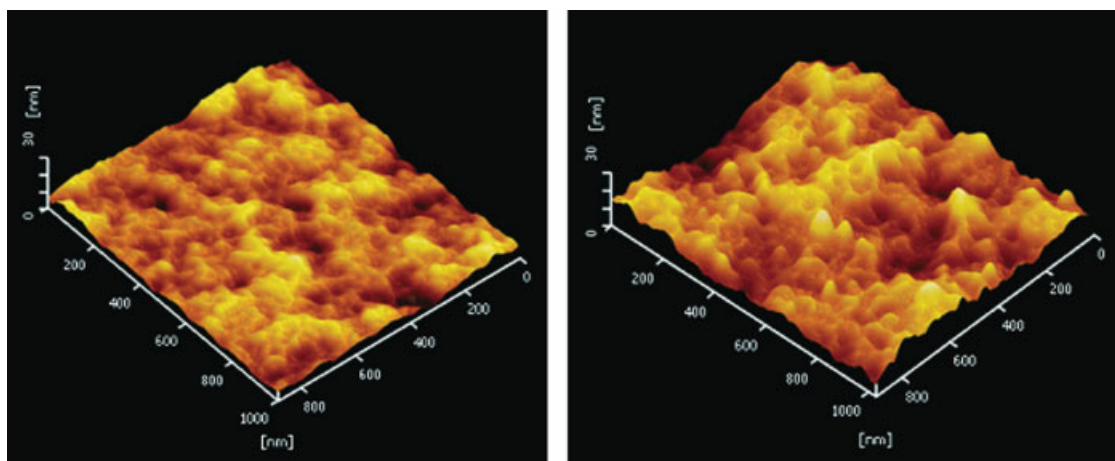


Figure 9 Three-dimensional AFM images of the outer surfaces of the hollow-fiber membranes: (a) without Tetronic 1307 and (b) with Tetronic 1307 (7 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

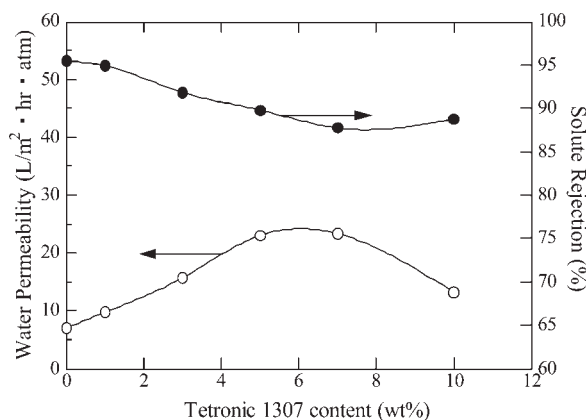


Figure 10 Effect of the Tetronic 1307 content on the water permeability and dextran rejection.

detailed study is necessary to clarify the reason for the roughness increase. Madaeni et al.²⁴ also reported such an increase in the surface roughness of UF membranes by the addition of surfactant.

Water permeability and solute rejection

Filtration experiments were carried out to study the permeability and solute rejection of the PES blend hollow-fiber membrane. The pure water permeability and dextran rejection are shown in Figure 10. As shown in this figure, when the Tetronic content was 1–7 wt %, the water permeability increased, whereas solute rejection decreased slightly. However, the addition of Tetronic 1307 of more than 7 wt % resulted in a decrease in the water permeability and an increase in the solute rejection. Water permeability was not changed during filtration. This indicated that the elution of Tetronic 1307 did not occur during the filtration because the elution of surfactant may have brought about an increase in the water permeability.

To enhance permeability, third components, such as PEG, poly(vinyl pyrrolidone) (PVP), and inorganic salts, are sometimes added in the casting solution. These are known as pore-forming agents. Kim and Lee⁷ investigated porous membrane formation by using a polysulfone/NMP/PEG casting solution. They suggested that the existence of PEG disturbed the aggregation of the polymer molecules in the top layer, which yielded a membrane with a more porous top layer. Tetronic 1307 can be dissolved in water and may act as a pore-forming agent and enhance permeation properties. This was the reason for the permeability increase with the addition of Tetronic 1307 amounts of less than 7 wt %. As shown in Figure 7(d), when the concentration of Tetronic 1307 was 10 wt %, a thick spongelike layer was formed near both the outer and inner surfaces. This probably led to a decrease in the permeability of the membrane prepared with addition of 10 wt % Tetronic 1307.

Membrane hydrophilicity and the retention ratio of Tetronic 1307 in the membrane

The contact angles of water on the outer surfaces of the membranes prepared with various Tetronic 1307 contents are shown in Figure 11(a). With increasing Tetronic content, the water contact angle became smaller. The decrease in the contact angles with increasing Tetronic 1307 content indicated that the membrane surface was more hydrophilic at higher Tetronic 1307 contents.

It was very important to know how much Tetronic 1307 remained in the resulting membranes. The retention ratios of Tetronic 1307 were measured by elemental analysis of the membranes and are plotted in Figure 11(b). In this figure, the actual concentration of Tetronic 1307 remaining in the membrane are also plotted. The retention ratio slightly decreased with increasing Tetronic 1307 content in the polymer solution. However, more than 70 wt % Tetronic 1307 still remained in the membrane, even in the case of high surfactant content. The actual Tetronic 1307 concentration the membrane increased with increasing initial Tetronic 1307 concentration. The high retention ratio was attributable to the higher molecular weight of Tetronic 1307. Tetronic 1307 may have been entangled with the PES polymer at the surface, which led to the higher retention ratio. The retention of Tetronic 1307 caused an increase in the hydrophilicity of the

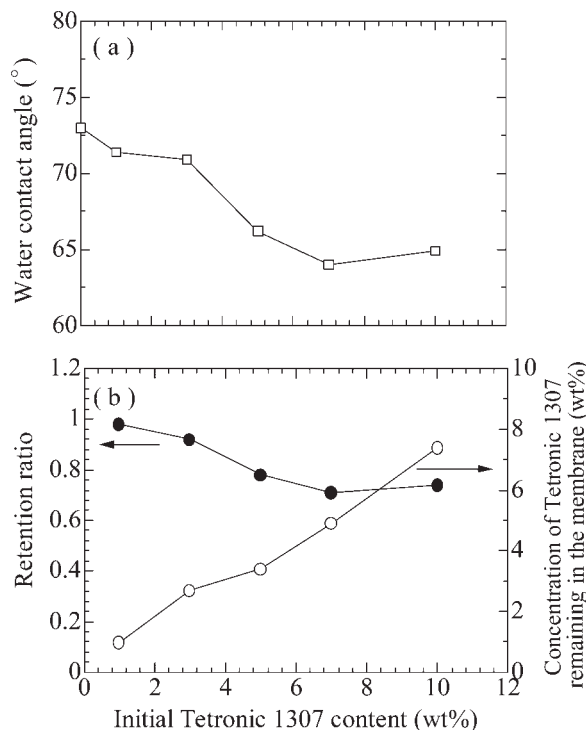


Figure 11 Effect of the Tetronic 1307 content on the water contact angle of the outer surface and the retention ratio of Tetronic 1307 in the membrane.

membrane surface. The membrane fouling results will be presented in the next article in our series of work.

CONCLUSIONS

Porous polymeric hollow-fiber membranes were prepared from a PES/NMP solution via the NIPS method. The effect of the addition of Tetronic 1307 on the performance and characteristics of the resulting membranes was investigated.

Light-scattering experiments were carried out to obtain kinetic data for the phase separation. With the addition of Tetronic 1307, delayed phase separation was observed, and the structure growth rate decreased.

All hollow-fiber membranes had asymmetric structures with a skin layer on the surface and fingerlike macrovoids inside the membrane. The addition of Tetronic 1307 was effective for enhancing the water permeability of the hollow-fiber membranes. Thus, this surfactant could act as one kind of pore-forming agent. The hydrophilicity of the membrane surface was also improved because of the high retention of Tetronic 1307 in the membrane.

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