Effect of Hypochlorite Treatment on Performance of Hollow Fiber Membrane Prepared from Polyethersulfone/*N*-Methyl-2-Pyrrolidone/Tetronic 1307 Solution

Nasrul Arahman,[1,2] Tatsuo Maruyama,[1] Tomohiro Sotani,[1] Hideto Matsuyama[1]

[1]*Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada-Ku, Kobe 657-8501, Japan*
[2]*Department of Chemical Engineering, Syiah Kuala University, Banda Aceh 23111, Indonesia*

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ABSTRACT: Polyethersulfone (PES) hollow fiber membrane was prepared by blending with nonionic surfactant Tetronic 1307 to improve its hydrophilicity. The membranes were posttreated by hypochlorite solution of 10, 100, 500, and 2000 ppm. The effect of hypochlorite treatment on the performance of PES membrane was investigated. Experimental results showed that the water permeability of treated membrane was two to three times higher than that of untreated membrane in case of blend membrane prepared from PES/*N*-methyl-2-pyrrolidone (NMP)/Tetronic 1307 solution. On the other hand, hypochlorite treatment has no effect on water permeability of the membrane prepared from PES/NMP solution. Elemental analysis and ATR–FTIR measurement results indicated that hypochlorite treatment led to decomposition and leaching out of Tetronic 1307 component from the membrane. The change of membrane surface structure by the hypochlorite treatment was confirmed by atomic force microscopy measurement. The hypochlorite treatment brought about no significant impact on the mechanical property of the membranes. This indicated that the hypochlorite treatment of PES membrane prepared with surfactant was a useful way to improve the water permeability without the decrease of membrane strength. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 687–694, 2008

Key words: polyethersulfone; hollow fiber membrane; nonsolvent-induced phase separation; hypochlorite treatment; tetronic 1307

INTRODUCTION

Microfiltration and ultrafiltration have been becoming an interesting methods for producing safety drinking water. These membrane processes have been attracting much attention throughout the world due to their highly efficient removal properties of particulates, virus, and bacteria. To be useful in industrial water treatment, membranes with high flux, high rejection, high mechanical stability, and good chemical resistance must be developed.[1] Polyethersulfone (PES) polymer is one of the polymers most frequently used in the preparation of microfiltrtion and ultrafiltration membranes due to its excellent chemical resistance, good thermal stability, and mechanical properties. Many researchers have focused their efforts to minimize hydrophobic property of PES, which is the main drawback of this polymer. To improve the hydrophilicity, PES membrane was blended with the hydrophilic polymer additives, such as polyvinylpyrrolidone (PVP), cellulose acetate phthalate (CAP), and Pluronic F127 (polymeric surfactant).[2–4] On the other hand, the addition of large amount of hydrophilic polymer additive on the membrane preparation solution resulted in decrease of water permeability.[5]

Hypochlorite posttreatment of PES membrane-containing polymeric additive has been introduced as a method to enhance water permeability. Qin et al.[2] reported in their investigation that water permeability of PES membrane blended with PVP was increased five times after soaked in hypochlorite solution of 4000 ppm for 48 h. Wienk et al.[6] also found the water permeability increase in PES/PVP blend membrane by increasing the immersing time in hypochlorite solution. They suggested that hypochlorite posttreatment may increase pore size of membrane by a reaction of hypochlorite with PVP.

In our previous work, new surfactant Tetronic 1307 was added to the membrane preparation solution as a membrane-modifying agent to improve the hydrophilicity of PES membrane.[7] Tetronic, which is commercially also available as Poloxamines, is a family of surfactants with X-shaped copolymers. It is

Correspondence to: H. Matsuyama (matuyama@kobe-u.ac.jp).

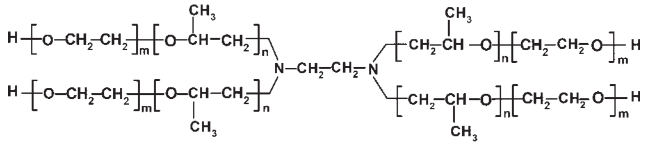

Figure 1 Molecular structure of Tetronic 1307.

formed by four poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) block chains bonded to an ethylene diamine central group. The sizes of both the PEO and PPO blocks can be independently modified giving rise to a wide range of HLB values. Tetronic 1307 is significantly hydrophilic (HLB > 24), with 72 unit of EO per PEO block.[8] The molecular structure of Tetronic 1307 are shown in Figure 1. This surfactant can adsorb strongly to the surface of hydrophobic materials via its PPO block.[9]

In this work, effect of hypochlorite treatment on the performance of PES/Tetronic 1307 blend membrane was investigated. Significant permeation improvement was achieved with keeping the hydrophilic property.

EXPERIMENTAL

Materials

The membrane material, PES (E6020) with M_w of 65,000 and surfactant Tetronic 1307 with a molecular weight of 18,000 and PEO content of 70 wt % were purchased from BASF, Germany. *N*-Methyl-2-pyrrolidone (NMP) used as solvent and sodium hypochlorite solution (chlorine content: 5%) used in the posttreatment of PES hollow fiber membrane were purchased by Wako Pure Chemical Industries, Japan. Dextran with molecular weight of 10,000 was purchased from Sigma (Germany). All chemicals were used without further purification.

Membrane preparation and hypochlorite posttreatment

Polymer solution consisting of 25 wt % PES and Tetronic 1307 with various concentration of 1, 3, 7, and 10 wt % was dissolved in NMP by stirring for 24 h at room temperature to obtain homogeneous dope solution. Hollow fiber membrane was prepared via nonsolvent-induced phase separation (NIPS) by a batch-extruder described in our previous work.[7] The hollow fiber was extruded from the spinneret and wounded on a take-up winder after entering into the coagulation bath to induced phase separation and solidify the membrane. The spinneret consists of outer and inner tubes, and their diameters are 1.00 and 0.70 mm, respectively. The polymer flow rate through the spinneret was controlled by a gear pump. Water was flowed into the inner tube to make lumen of the hollow fiber. The membrane preparation conditions were fixed to be constant for all cases as summarized in Table I.

The obtained membrane was finally treated by hypochlorite solution. Five pieces of hollow fiber membrane with length of 34 cm were cut in two series of 17-cm parts. Five pieces of 17-cm length in one series were directly measured for several membrane characterizations such as membrane morphology, membrane hydrophilicity, membrane roughness, filtration performance, mechanical properties, and chemical composition. On the other hand, five pieces in other series of hollow fiber membranes were immersed in hypochlorite solution at 50°C. The pH of hypochlorite solution was fixed at 11.5, and concentrations were changed from 10, 100, 500, and 2000 ppm. After 3-h immersing in hypochlorite solution, the membranes were rinsed in deionized water for 24 h and subsequently measured for several characterizations in the same manner with untreated membrane.

Ultrafiltration performances

Ultrafiltration performance of the resulting membranes were characterized by measuring water permeability of deionized water and solute rejection of dextran. The filtration apparatus was designed as laboratory scale of cross-flow filtration with similar method that described by Iwata et al.[10] Deionized water was forced to permeate from the inside to the outside of the hollow fiber membrane. The transmembrane pressure could be applied by adjusting the pressure valve close to the release side, and the average of the readings of the two pressure gauges was taken as the feed pressure. The pressure was ranged from 0.05 to 0.1 MPa. The water permeability was calculated on the basis of the inner surface area of the hollow fiber membrane.

For rejection test, the solution of 1 wt % dextran with average molecular weight of 10,000 was used as the feed solution. The filtration procedure was the same as that in water permeability experiment. Solute rejection of the membrane was obtained by the

TABLE I
Preparation Conditions for Hollow Fiber Membrane

Polymer flow rate (m/min)	3.20
Internal coagulant flow rate (m/min)	10.4
Take-up speed (m/min)	11.0
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

measurement of refractive index of pure water, feed dextran solution, and permeate dextran solution by a refraction index measurement apparatus (Model 3, Atago, Japan). Rejection of the hollow fiber membrane was calculated by using 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 indexes of permeate dextran solution, feed dextran solution, and pure water, respectively.

Water contact angle

Water contact angle measurement was performed to observe the degree of membrane hydrophilicity by a contact angle meter (CA-A, Kyowa Interface Science, Japan). Two micrograms of water droplet were dropped on the outer surface of hollow fiber membrane. Each contact angle was measured for 10 times, and an average value was calculated.

Elemental analysis

In the membrane preparation via NIPS method, some of Tetronic 1307 added in the polymer solution may be flowed out from the PES blend membrane during the solidification in coagulation bath. Elemental analysis was conducted to analyze the amount of surfactant remained in the blend membrane. The ratio of the amount of surfactant remained in the membrane to the initial surfactant amount is defined as a retention ratio. Retention ratio was calculated based on the ratio of hydrogen to carbon measured by a chemical element analyzer (Sumigraph NCH-21, SUMIKA Analysis Center Co., Japan) by using eq. (2):

$$\text{Retention ratio} = \left(\frac{X}{Y}\right) \times 100\,\% \quad (2)$$

where Y is the initial amount of Tetronic 1307 added to the polymer solution, and X is the amount of Tetronic 1307 remained in the membrane. First, we measured the ratios of hydrogen to carbon of PES membrane and Tetronic 1307. Then the ratio of the PES blend membrane with Tertonic 1307 was measured. By using these three ratios, the amount of Tetronic 1307 remained in the membrane was calculated. Thus, the retention ratio was obtained.

ATR–FTIR analysis

To observe the chemical structure changes of PES and PES blend membranes before and after treatment by hypochlorite solution, the attenuated total reflection Fourier transform infrared (ATR-FTIR) measurement was carried out by a FTIR-8100A Fourier transform infrared spectrophotometer (Shimadzu, Japan). The outer surface of PES and PES blend membranes were directly analyzed after dried in vacuum oven at 70°C for 24 h. FTIR measurement of Tetronic 1307 was also carried out by KBr method. KBr tablet with diameter size of 13 mm was used to analyze the functional group of Tetronic 1307 by FTIR measurement. IR spectra of the membranes were recorded in the wavenumber ranging between 400–4000 cm^{-1} at room temperature.

Membrane morphology

The morphologies of PES hollow fiber membranes before and after treatment by hypochlorite solutions were observed by a Scanning Electron Microscope (SEM, *S*-800, Hitachi Co., Japan) with an accelerating voltage of 20 kV. The membrane sample was firtsly dried in a freeze dryer (FD-1000, EYELA, Japan) for about 3 h. For the cross section observation, the freeze-dried hollow fiber membranes were fractured in liquid nitrogen. Atomic force microscopy (AFM, SPA400, SII NanoTechnology Inc., Japan) was used to obtain the morphology of membrane outer surfaces. In this work, the membrane surfaces were imaged in a scan area of 1 μm x 1 μm. The average values of mean surface roughness (Ra) were calculated from ten images of random samples.

Mechanical properties

The tensile strength and elongation of the PES hollow fiber membranes was measured with a tensile apparatus (AGS-J, Shimadzu). The membrane was fixed vertically between two pairs of tweezers with the length of 50 mm. Then the membrane was extended at a constant elongation rate of 50 mm/min until it was broken. The average value of tensile strength and elongation was calculated from 10 measurements for each membrane.

RESULTS AND DISCUSSION

Ultrafiltration performances

As mentioned in the experimental section, filtration performances of obtained membranes were investigated by measuring water permeability and solute rejection. Figure 2 shows the effect of initial Tetronic 1307 content on the water permeability of the PES blend membrane treated by hypochlorite solution of 2000 ppm. This Tetronic 1307 content in the abscissa means the initial concentration in the dope solution. The water permeabilities of untreated membrane were also shown as comparison. As shown in Figure 2, the water permeability of PES blend membrane with 7 wt % Tetronic 1307 treated with hypochlorite solution was about two times higher than that of the untreated membrane. Moreover, when the initial Tetronic 1307 concentration was 10 wt %, the water permeability of the treated membrane was about three times higher than that of untreated membrane. On the other hand, when no Tetronic 1307 was added to the dope solution, the water permeability was hardly changed after the hypochlorite treatment. Thus, the improvement in the water permeation can be achieved only in the case of Tetronic 1307 addition.

Effect of the hypochlorite solution concentration on the water permeabilities of PES membranes prepared from PES/NMP system and from PES/NMP/7 wt % Tetronic 1307 system are shown in Figure 3. The membranes were treated in various hypochlorite concentrations of 10, 100, 500, and 2000 ppm. For the membrane prepared from PES/NMP/Tetronic 1307 system, the initial water permeability before the treatment is denoted as dashed line in Figure 3. For PES original membrane prepared from PES/NMP system, the water permeabilities were almost the same as initial value even after the treatment with high concentration of hypochlorite solution. Thus, hypochlorite treatment brought about no changes in water permeability of PES original membrane. PES is well known as the material with high chemical stability, and thus, the membrane structure was hardly changed by this hypochlorite treatment. The water permeability of membrane prepared from PES/NMP/Tetronic 1307 system increased drastically even by the treatment with low concentration of hypochlorite concentration (100 ppm). During the contact with hypochlorite solution, some parts of Tetronic 1307 are decomposed and eventually leached

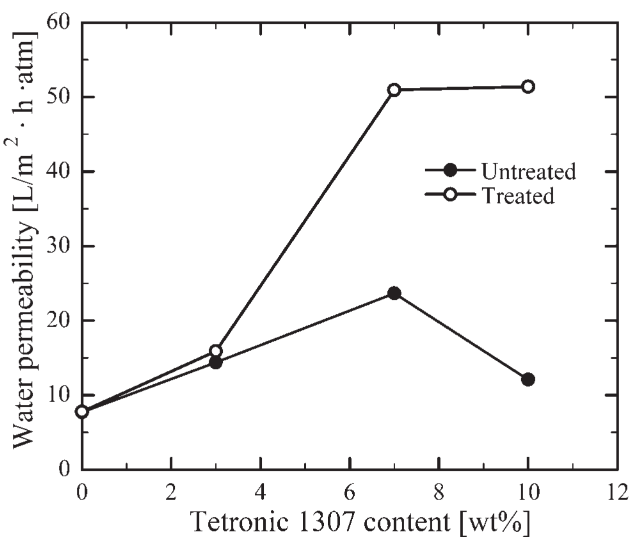

Figure 2 Effect of Tetronic content on water permeability of PES membrane treated by hypochlorite solution of 2000 ppm.

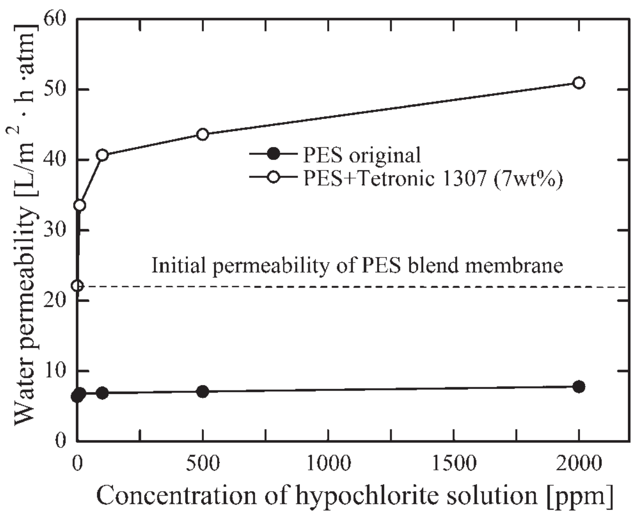

Figure 3 Effect of hypochlorite solution concentration on water permeability.

from the membrane, resulting in more porous structure. This is the reason that the water permeability increased after the treatment by hypochlorite solution in case of the membrane prepared from PES/NMP/Tetronic 1307 system. Because the PES original membrane does not contain Tetronic 1307, no permeability improvement could be observed. Wienk et al.[6] investigated the effect of hypochlorite treatment on PES membrane blended with PVP and found that water permeability increased with immersing time. They proposed that hypochlorite reacts with PVP, causing the chain scission of polymer and ring opening of the pyrrolidone ring of the PVP molecule. They also mentioned that hypochlorite can attack ether bond and hydroxyl group. Tetronic 1307 has the aliphatic ether bond, as shown in Figure 1. This bond may be decomposed by the hypochlorite treatment. However, further detailed investigation is necessary to clarify the chain scission.

Figure 4 shows the effect of Tetronic 1307 content in the polymer solution on solute rejections of the obtained membranes. The rejections for membranes before and after treatment by hypochlorite solution of 2000 ppm are plotted in this figure. Solute rejection of dextran with molecular weight of 10,000 did not decrease significantly by the hypochlorite treatment. It indicates that hypochlorite treatment of PES/Tetronic 1307 blend membrane was no substantial in deterioration of the membrane structure.

Membrane hydrophilicity

Water contact angle measurement on membrane outer surface was carried out to observe hydrophilicity property of PES original and PES blend membrane before and after treatment by hypochlorite solution of 2000 ppm. The results are shown in Table II. PES

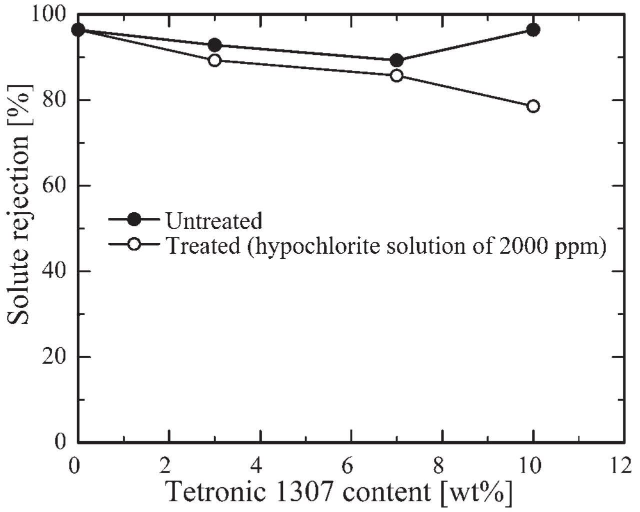

Figure 4 Effect of Tetronic 1307 content in the polymer solution on solute rejection of the obtained membranes. Dextran with molecular weight of 10,000 was used as solute.

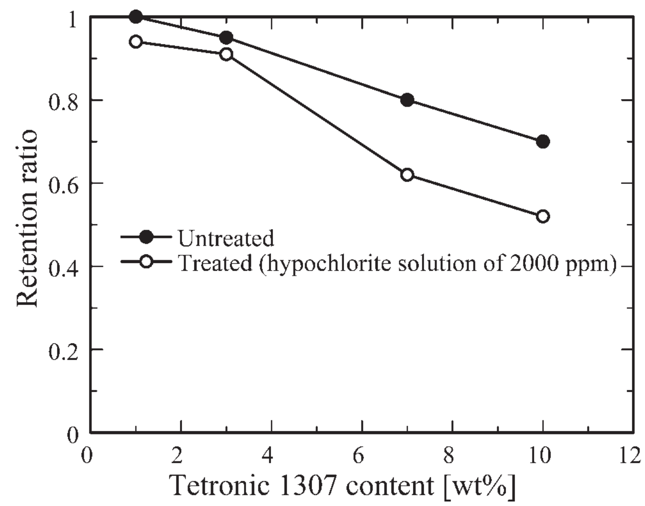

Figure 5 Effect of hypochlorite treatment on retention ratio of Tetronic 1307.

original membrane prepared from PES/NMP system showed the higher water contact angle, indicating that the membrane was hydrophobic. In addition, the contact angle was hardly influenced by the hypochlorite treatment. Water contact angle decreased with the increase of Tetronic 1307 content. This means that the addition of Tetronic 1307 was useful to improve the hydrophilicity.[7] The decrease of water contact angle was attributed by hydrophilic property of PEO segment contained in Tetronic 1307, because Tetronic 1307 is significantly hydrophilic (HLB > 24).[8] Also, in the case of the Tetronic 1307 addition, the hypochlorite treatment has no significant effect on membrane hydrophilicity.

The degree of hydrophilicity of PES blend membrane can be related with the amount of Tetronic 1307 remained in the prepared membranes. Elemental analysis of the membranes was carried out to confirm retention ratios of Tetronic 1307 in the membrane. The obtained retention ratios are presented in Figure 5. As shown in this figure, the retention ratio slightly decreased with increasing Tetronic 1307 content. After treatment by hypochlorite solution of 2000 ppm, the retention ratio was about 20% decreased in the case of the PES membranes blended with 7 and 10 wt % Tetronic 1307. This decrease of the retention ratio is attributed to the decomposition and leaching of Tetronic 1307, as described earlier. However, even after the hypochlorite treatment, Tetronic 1307 was still remained in the membrane. This is the reason for keeping the membrane hydrophilicity after the treatment.

TABLE II
Water Contact Angle of Membrane Outer Surface Before and After Treatment by Hypochlorite Solution of 2000 ppm

Membrane	Water contact angle (°) Untreated	Water contact angle (°) Treated
PES	75.9	75.2
PES/Tetronic 1307 (1 wt %)	74.5	74.7
PES/Tetronic 1307 (3 wt %)	68.8	68.4
PES/Tetronic 1307 (7 wt %)	63.0	62.5
PES/Tetronic 1307 (10 wt %)	63.5	61.6

ATR–FTIR spectroscopy

According to the ultrafiltration performance, the water permeability of PES blend hollow fiber membrane was improved after the hypochlorite treatment. ATR–FTIR measurement was carried out to investigate the chemical structure of PES hollow fiber membrane. The results are shown in Figure 6. Curves 1 and 2 are the IR spectra of PES original membrane before and after the treatment with hypochlorite solution of 2000 ppm, respectively. The original PES membrane was characterized by the strong bands at 1577 and 1460 cm^{-1} attributed to aromatic bands.[11–14] The IR spectrum of PES original membrane before the treatment was almost the same as that after the treatment, which indicated that the hypochlorite treatment in this work did not cause the decomposition of chemical structure. Bégoin et al.[15] reported the treatment of PES membrane by hypochlorite solution of 7600 mg L^{-1} at pH 11.5. To discuss the spectra change after the treatment, they used the relative absorbance, which is defined as the ratio of the band height at a given wavenumber to that at reference wavenumber. For the data shown in Figure 6, the relative absorbance at the given

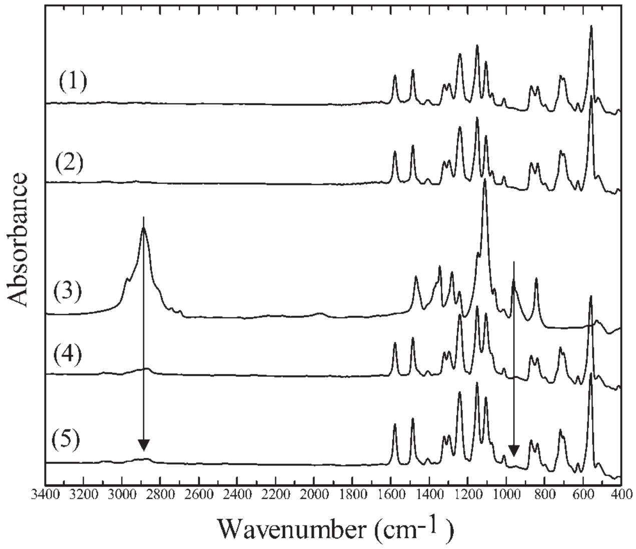

Figure 6 ATR–FTIR results. (1) PES original membrane, (2) PES original membrane (treated), (3) Tetronic 1307, (4) PES + 7 wt % Tetronic 1307, and (5) PES + 7 wt % Tetronic 1307 (treated).

wavenumber (x cm^{-1}) to 1577 cm^{-1} was calculated based on eq. (3):

$$\text{Relative absorbance} = H_x/H_{1577} \quad (3)$$

where H_x is the band height at x cm^{-1} and H_{1577} represents the band height at 1577 cm^{-1}. The results are summarized in Table III. The relative absorbances in the treated membrane are the same as those in the original membrane.

Curve 3 in Figure 6 is the IR spectrum of Tetronic 1307. A large peak appears in the band between 2900 and 2650 cm^{-1} and 1200–1000 cm^{-1} attributed to the stretching vibration of methyne C—H and C—O—C of aliphatic ether bond, respectively.

The spectrum of the PES blend membrane with Tetronic 1307 is shown in curve 4. In this spectra, the weak bands at 2870 and 951 cm^{-1} in corresponding to the stretching vibration of methyne C—H and skeletal C—C vibration of Tetronic 1307 can be recognized. Arrows in Figure 6 are located in these two wavelengths. Because these peaks were absent in PES original membrane (curve 1), the existence of these peaks denotes the remaining of Tetronic 1307 in the membrane. Curve 5 shows the spectrum of the PES blend membrane treated by hypochlorite solution of 2000 ppm. In this spectrum, the peaks at 2870 and 951 cm^{-1} are also observed. This is also the evidence that Tetronic 1307 was still remained after the hypochlorite treatment. The relative absorbance at 2870 cm^{-1} decreased from 0.40 to 0.3 after the treatment, whereas the other relative absorbances were not changed (Table III). This indicates that some of Tetronic 1307 was leached out from blend membrane during immersing in hypochlorite solution due to the decomposition.

Membrane morphology

To understand the effect of hypochlorite treatment on the pore structures of the PES membrane, SEM and AFM observations were carried out before and after treatment by hypochlorite solution. Figure 7 shows SEM images of hollow fiber membrane near outer surface before and after the treatment for both membranes prepared from PES/NMP and PES/NMP/Tetronic 1307 solutions. For both membranes, the membrane pore structure was not changed after the hypochlorite treatment. As shown in Figures 2 and 3, the water permeability of PES-Tetronic 1307-blend membranes increased by the treatment. The ATR–FTIR analysis showed the leaching out of Tetronic 1307 by the treatment. However, no clear morphology change was observed in this magnification of SEM. Qin et al.[2] founded that the pore size of PES/PVP membrane was dramatically increased after treated with hypochlorite solution of 4000 ppm for 48 h. They also reported that the thickness of the outer skin layer apparently decreased after soaked in hypochlorite solution of 4000 ppm. On the other hand, the membrane morphology did not change through short time of hypochlorite treatment, as reported by Jung et al.[16] The degree of membrane morphology change is dependent on the hypochlorite treatment condition.

The detailed investigation about the surface structure was carried out by the AFM measurement.

TABLE III
Relative Absorbances in IR Spectra

Wavenumber (cm^{-1})	Assignment	PES original H_x/H_{1577}	PES original (treated) H_x/H_{1577}	PES + Tetronic 1307 H_x/H_{1577}	PES + Tetronic 1307 (treated) H_x/H_{1577}
1577	Aromatic ring stretch	1.00	1.00	1.00	1.00
1485	Aromatic ring stretch	1.20	1.20	1.14	1.14
1323	SO_2 stretch	0.66	0.66	0.73	0.71
1240	C—O ether	1.40	1.40	1.40	1.40
1150	SO_2 stretch	1.73	1.73	1.62	1.62
705	C—S stretch	0.83	0.83	0.71	0.70
2870	Methyne C—H stretch	–	–	0.40	0.30

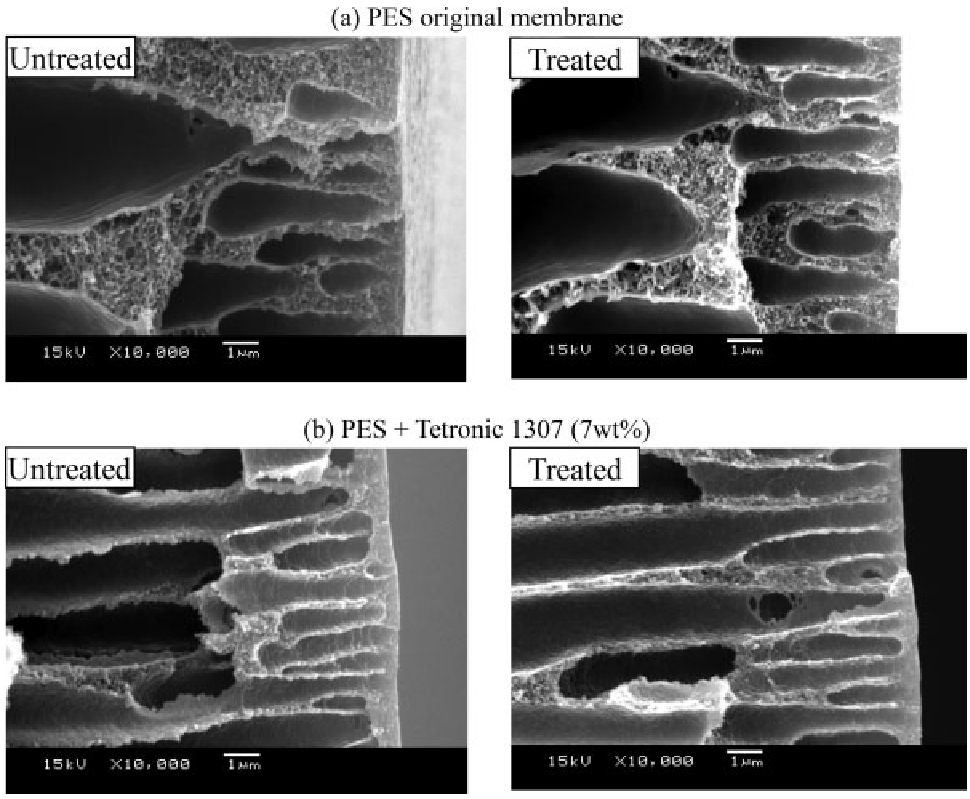

Figure 7 SEM images of PES hollow fiber membranes before and after treatment by hypochlorite solution of 2000 ppm.

Figure 8 shows the three-dimensional AFM images on the outer surface of PES hollow fiber membrane prepared from PES/NMP/Tetronic 1307 (7 wt %) solution. Hypochlorite treatment brought about the decrease of nodule size on the outer surface. The mean roughness (R_a) of membrane was obtained from 10 images of random sample and the average values were calculated. The mean roughness decreased from 2.2 nm to 1.2 nm by the hypochlorite treatment. Thus, the morphology change in nanoscale, which can be detected not by SEM measurement but by AFM measurement, occurred by the treatment, which brought about the increase of the water permeability.

Mechanical properties

The tensile strength and elongation of PES membranes prepared from PES/NMP and PES/NMP/Tetronic 1307 system before and after the hypochlorite treatment are shown in Table IV. The mechanical properties of the blend membrane are lower than those of original membrane. However, hypochlorite treatment hardly gave a significant impact on the

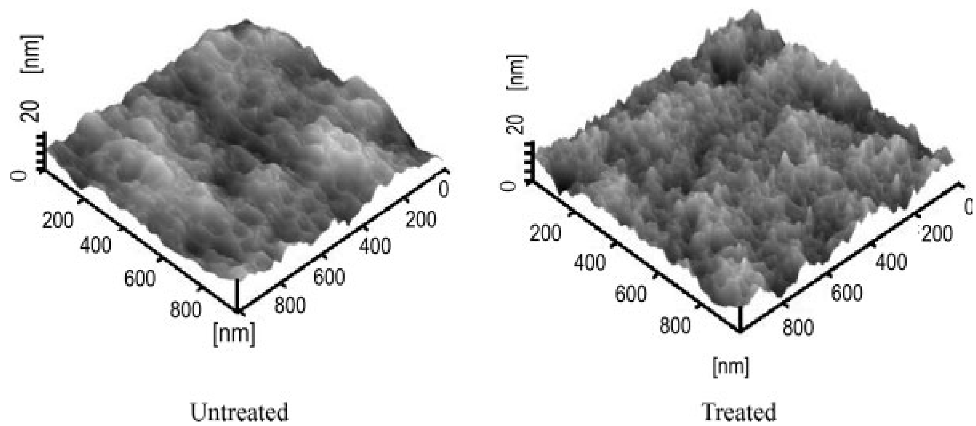

Figure 8 AFM image of outer surface of PES blend membranes with Tetronic 1307 (7 wt %) before and after treatment by hypochlorite solution of 2000 ppm.

TABLE IV
Mechanical Properties of PES Hollow Fiber Membrane Before and After Treatment by Hypochlorite Solution of 2000 ppm

Membrane sample	Tensile strength (MPa)	Elongation (%)
PES	18.0	107
PES (treated)	16.7	105
PES/Tetronic 1307, 7 wt %	8.38	64.7
PES/Tetronic 1307, 7 wt % (treated)	8.13	52.7

mechanical property of both membranes prepared from PES/NMP and PES/NMP/Tetronic 1307 system. This indicates that the hypochlorite treatment of PES membrane in this work did not cause the deterioration of the membrane even though the increase of the water permeability. Similar observations were reported by Causserand et al.[17] They mentioned that the mechanical properties of polysulfone membrane was not changed after soaked with sodium hypochlorite solution of 100 ppm for 15 days. Zondervan et al.[18] also concluded from their analysis that the mechanical properties of PES ultrafiltration membrane did not change so much after exposure to hypochlorite solution.

CONCLUSIONS

Hydropihilic PES hollow fiber membrane was prepared by blend with Tetronic 1307. The effect of hypochlorite treatment on the performance of PES membrane was investigated. The membranes were treated by various concentrations of hypochlorite solutions of 10, 100, 500, and 2000 ppm. The water permeability of the membrane increased significantly even by the treatment with low concentration of hypochlorite solution. The mechanical strength hardly changed after the treatment.

Elemental analysis and ATR–FTIR measurement showed the hypochlorite treatment brought about the decomposition and leaching out of some Tetronic 1307 component from the membrane. However, the surface hydrophilicity was still kept even after the treatment. The change of surface roughness in nanoscale by the treatment was confirmed by the AFM measurement.

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