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Research Paper

PERFORMANCE OF POLYETHERSULFONE /TETRONIC 1307 HOLLOW FIBER MEMBRANE FOR DRINKING WATER PRODUCTION

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Abstract: Polyethersulfone (PES) hollow fiber membrane was prepared with improved hydrophilic property by addition of polymeric additive surfactant Tetronic 1307. The objective of this study is to investigate effect of addition of Tetronic 1307 on the filtration performance of PES hollow fiber membrane. The filtration performances of membrane were studied by using deionized water and bovine serum albumin (BSA) as a model protein in order to analyze membrane fouling. Experimental results indicated that the membrane with Tetronic 1307 showed higher fouling resistance in the comparison with original PES membrane. Flux recovery of PES membrane with Tetronic 1307 was three times higher than that of orginal PES membrane. The membrane morphology before and after fouling by BSA solution was observed by use a Scanning Electron Microscope. A cake layer formation on the surface of PES original membrane was clearly observed, while it was not observed on the surface of PES blend membrane.

Keywords: Membrane fouling, PES hollow fiber membrane, Tetronic 1307

INTRODUCTION

Membrane filtration is an attractive method for drinking water production, because it is capable of disinfecting water and removing its turbidity at relatively low pressure. In recent years, ultrafiltration has recognized as an effective method in water purification process. The advantages of membrane filtrations are that they are capable of removing a wide range of substances, and able to produce water with constant quality. Membrane filtrations offer relative simplicity of operation and low energy requirements for operation and maintenance in comparison to conventional treatment. Membrane systems tend to be more compact (typically occupying 33% less space), lend themselves to automation, and have lower chemical usage (less chemical cost, and reduced waste generation) [1-3]. Many researchers have focused their investigation on the production of membrane with high performance for this application. Polyethersulfone (PES) are well known in excellent chemical resistance, good thermal stability and mechanical properties.

This polymer is widely used in membrane preparation for various applications [4-6]. On the other hand, pure PES membrane is hydrophobic and low fouling resistance, which is the main drawback in practical application. Improving hydrophiclity of membrane surface has been reported as a method to reduce membrane fouling. In order to improve the hydrophilicity, PES membrane was blended with the hydrophilic polymer additives, such as polyvinylpyrrolidone (PVP), poly(ethylene glycol) (PEG), cellulose acetate phthalate (CAP) and Pluronic F127 (polymeric surfactant). Membrane formation and its hydrophilicity properties by addition of a third component in the polymer solution such as PVP, PEG, CAP, and Pluronic F127 were reported in the journal [7-10].

Very few studies have been reported about the hollow fiber membrane formation from the blending polymer system via non-solvent induced phase separation (NIPS) process. In this work, polymeric surfactant Tetronic 1307 was used as a membrane-modifying agent in order to improve the hydrophilicy of PES hollow fiber membrane, and effect of addition of Tetronic 1307 on the membrane fouling was investigated. The Tetronic is a family of surfactants based on X-shaped copolymers formed by four poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) block chains bonded to an ethylene diamine central group [11]. As far as we know, this is the first work that blend PES/NMP/Tetronic 1307 hollow fiber membranes were prepared by NIPS procedure.

MATERIALS AND METHODS

Hollow fiber membranes were prepared via non-solvent induced phase separation (NIPS) by a batch-extruder as described previously [12-13]. Dope solutions were prepared by dissolving PES and Tetronic 1307 in N-Methyl-2-pyrrolidone (NMP) by stirring for 24 h at room temperature. PES concentrations in dope solution were 22, and 25 wt% for PES/NMP and PES/NMP/Tetronic 1307 system, respectively. 7 wt% of Tentronic 1307 was added in the PES/NMP/Tetronic 1307 system. The obtained membrane was measured for several membrane characterizations such as membrane morphology, water permeability and fouling resistance. Membrane morphologies (whole cross-section, enlarged cross-section, inner and outer surface) were observed by a Scanning Electron Microscope (SEM, S-800, Hitachi Co., Japan) with an accelerating voltage of 20 kV. The membrane sample was firstly 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.

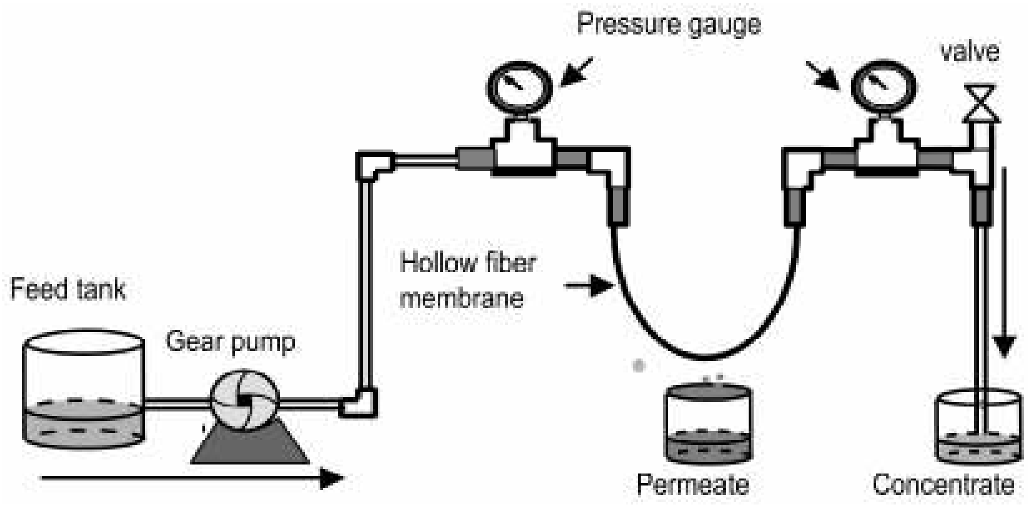


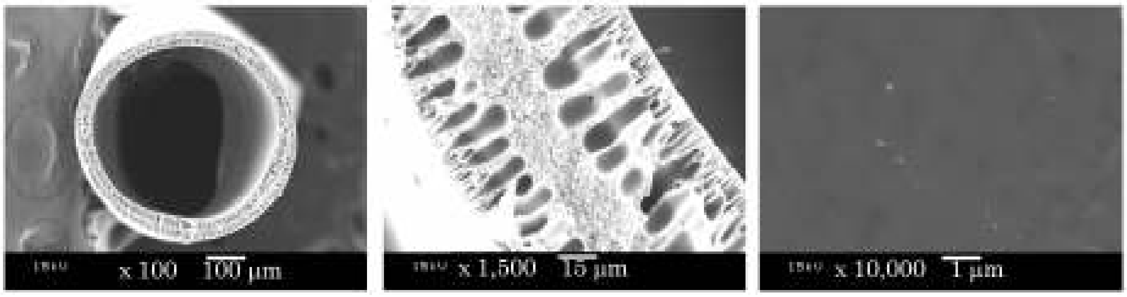
Fig. 1: Schematic diagram of ultrafiltration apparatus.

The schematic laboratory-scale apparatus used for ultrafiltration are shown in Fig 1. Filtration solution 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 (ranged from 0.05 to 0.1 MPa) was taken as the feed pressure. The flux of membrane was calculated on the basis of the inner surface area of the hollow fiber membrane. Bovine serum albumin (BSA) with concentration of 1 mg/ml was used as a model protein in order to analyze the fouling phenomena. The pH of the solutions was adjusted by using sodium dihydrogenphosphate at 7.0 $\pm$ 1. Permeate fluxes through the hollow fiber membrane were obtained by collecting and weighing permeate every 5 minutes until the end of filtration.

RESULTS AND DISCUSSION

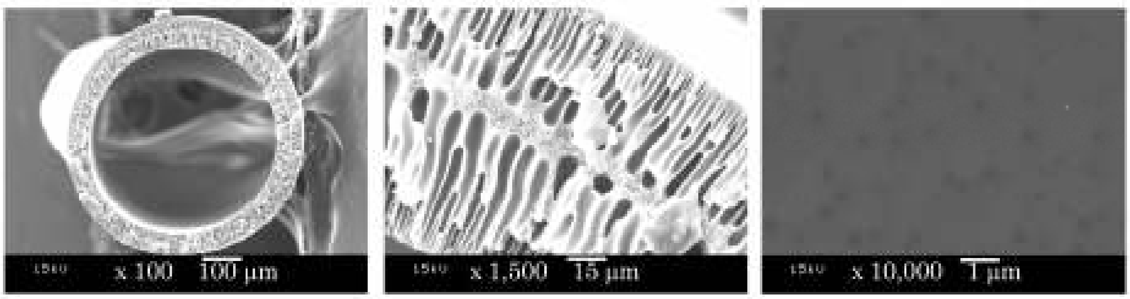
In this study, polyethersulfone hollow fiber membranes were prepared via non-solvent induced separation (NIPS) method with different polymer concentration, in order to obtain the same initial membrane fluxes. The study was focused on the ability of PES membrane to reduce membrane fouling in order to obtain high flux of membrane. Figure 2 shows SEM images of hollow fiber membrane (whole cross-section, enlarged cross-section and outer surface) prepared from PES/NMP and PES/NMP/Tetronic 1307 (7wt%) solutions.

(a). Membrane prepared from PES/NMP solution



Whole cross-section Enlarged cross-section Outer surface

(b). Membrane prepared from PES/NMP/Tetronic 1307 solution



Whole cross-section Enlarged cross-section Outer surface

Fig. 2: SEM images of PES hollow fiber membranes.

As shown in Fig. 2, in both systems, the membranes had typical structures of NIPS membranes with skin layer near outer and inner surface and finger-like macrovoids structure inside the hollow fiber membrane. The membrane prepared in PES/NMP system showed a larger sponge structure and small finger-like macrovoids**.** The number and length of finger-like macrovoids increased with addition of Tetronic 1307 in the polymer solution. The sponge-type structure in the center of the membrane also decreased with addition of Tetronic 1307. The typical structure of membrane formation by NIPS method are reported elsewhere [12, 14-15].

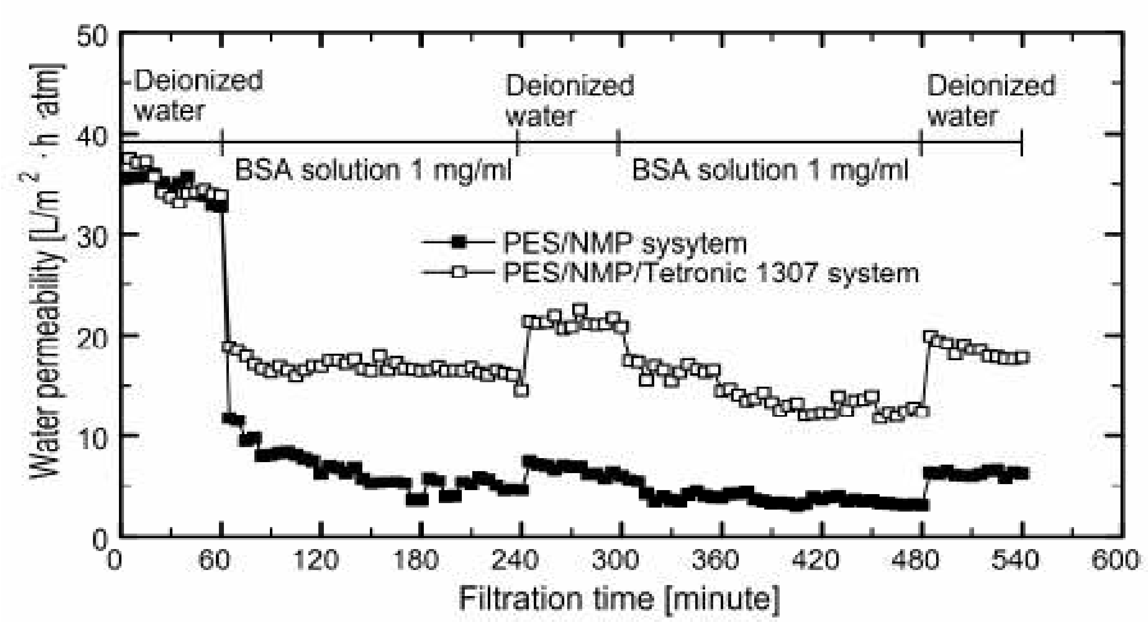


Fig. 3: Time course of water permeabilities.

Figure 3 shows the ultrafiltration performance of hollow fiber membrane prepared from PES/NMP, and PES/NMP/Tetronic 1307 (7wt%) system. The filtration experiments were performed in first one hour by using deionized water as a feed solution. The fluxes of both membranes were almost the same at the beginning of filtration, as shown in Fig.3. BSA solution of 1mg/ml was used as a feed solution for the next three hours of filtration experiment. In that time, flux of membrane prepared from PES/NMP system was drastically decreased to be about 30% based on initial flux of in the beginning of filtration. In the same condition, flux of membrane prepared form PES/NMP/Tetronic 1307 (7wt%) was about two times higher than that of PES/NMP system. The decreasing of flux at the initial filtration of BSA solution was attributed by adsorption or convective deposition of BSA on the membrane surface. Some protein molecules of BSA adsorbed on the pore surface of membrane and in consequence the formed cake layer caused the decrease of flux. To enhance the fouling resistant, third components such as CAP, Pluronic and inorganic salts were sometimes added in the casting solution. These are known as membrane modifying agent. Rahimpour and Madaeni investigated the fouling phenomena by using PES/dimethylacetamide (DmAc)/Cellulose acetate phtalate (CAP) solution [8]. They reported that fouling resistance of PES flat membrane improved was about two times by addition of CAP on the casting solution.

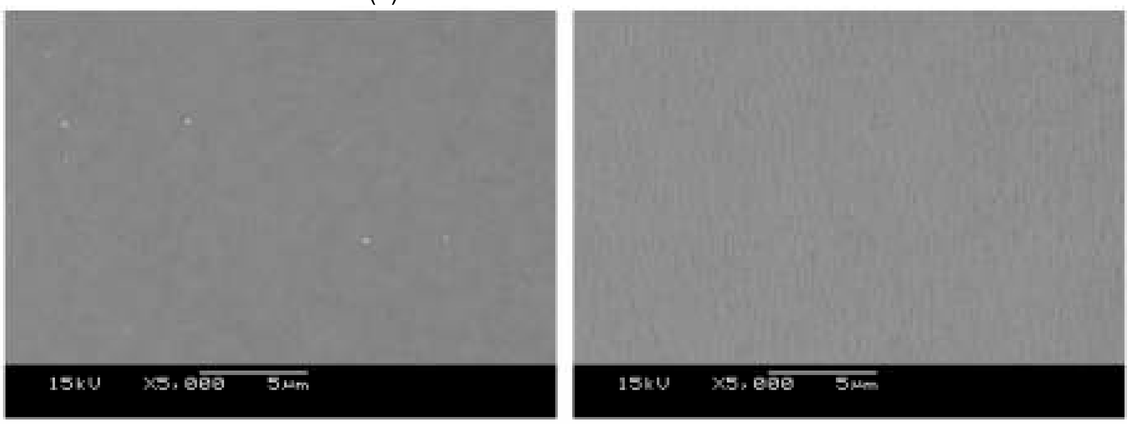
After three hour filtration with BSA solution, the membrane was cleaned by flowing deionized water with low pressure in the same direction of BSA filtration for 1 hour. Thus, deionized water was subsequently used as a feed solution in the third step of filtration experiment. Flux recovery ratio (FRR) of membrane was evaluated by equation (1).

$$\text{Flux recovery} = \left(\frac{J}{J_0}\right) x 100\% \qquad (1)$$

Here, *J* is deionized water flux of cleaned membrane after fouled by BSA solution, and J_0 is the initial deionized water flux of virgin membrane. Flux recovery ratios were 19 and 57 % for membrane prepared from PES/NMP and PES/NMP/Tetronic 1307, respectively. FRR of PES blend membrane was about three times larger than that of original PES membrane. This indicated that Tetronic 1307 was effective in enhanced fouling resistant of PES membrane. High FRR of membrane prepared from PES/NMP/Tetronic 1307 is attributed by hydropilicity properties of PEO segment contained in Tetronic 1307. Tetronic 1307 is high hydrophilic surfactants with hydrophile-lipophil balance (HLB >24)[16]. Similar investigation was done by Wang and co workers [17]. They prepared the hydrophilic PES flat membrane by addition of surfactant Pluronic F127 on the casting solution, and founded the FRR increase with an increase of the Pluronic F127 contents.

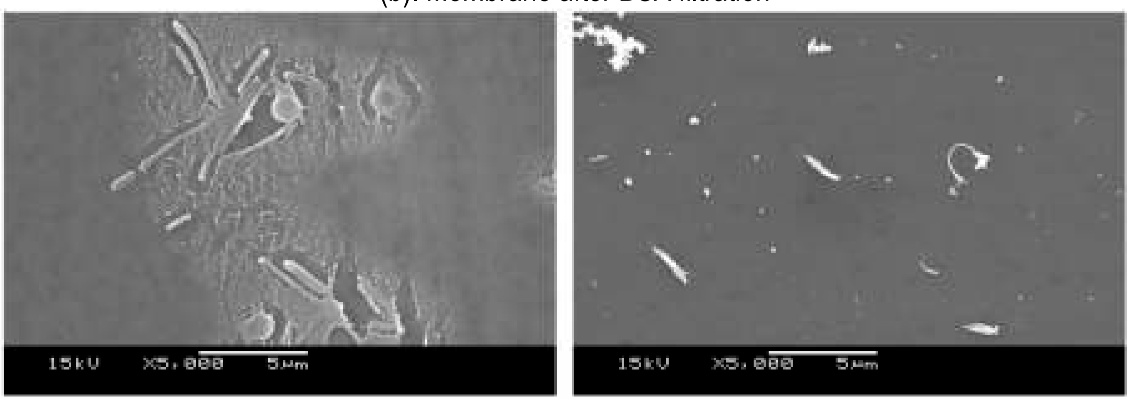
In the fourth step of filtration experiment, BSA solution of 1 mg/ml was again used as feed solutions for next three hours and deionized water were used in the final step of filtration. Flux performances of both membranes showed the similar trends observed in the second step of BSA filtration. Since the BSA solutions were flowed through the inner side of hollow fiber membrane, the inner surface structures of the membranes were observed by SEM measurement. Figure 4 showed SEM images of membrane inner surfaces before and after BSA filtration for both membranes prepared with PES/NMP system and PES/NMP/Tetronic system.

(a). Membrane before BSA filtration



PES/NMP system OPES/NMP/Tetronic 1307

(b). Membrane after BSA filtration



PES/NMP system PES/NMP/Tetronic 1307 system

Fig. 4: SEM images of inner surfaces PES hollow fiber membranes before and after BSA filtration.

The small particles or aggregate appeared on the inner surface of membrane prepared from PES/NMP/Tetronic 1307 system. This indicated some protein molecules adsorbed or aggregated on the membrane surface. In contrast, the inner surface of membrane prepared from PES/NMP system was covered with thick cake layer of BSA. An existence of BSA residuals on the membrane surface suggests that BSA is actually easily adsorbed in the surface of hydrophobic layer [18]. This can actively contributes to the formation of a cake layer. The PES/NMP membrane is low hydrophilicity with contact angle about 75^o, and PES/NMP/Tetronic 1307 is high hydrophilcity with contact angle about 65^o [13]. The existence of PEO segment of Tetronic 1307 was attributed to the increase of hydrophilicity of membrane prepared from PES/NMP/Tetronic 1307 system, resulting in reduced protein adsorption on the membrane surface.

CONCLUSIONS

PES hollow fiber membrane was prepared via non-solvent induced phase separation process, and effect of addition of Tetronic 1307 on the membrane fouling was investigated. Ultrafiltration experiments were carried out by used deionized water and BSA solution. The membrane prepared from PES/NMP system showed that the flux decreased significantly when the BSA solution was filtrated, while flux of membrane prepared from PES/NMP/Tetronic 1307 system was higher. Flux recovery ratios were 19 and 57 % for membrane prepared from PES/NMP and PES/NMP/Tetronic 1307, respectively. This indicated the membrane prepared from PES/NMP/Tetronic 1307 system was higher fouling resistance than that membrane prepared from PES/NMP system. Addition of Tetronic 1307 on the polymer system brought about the improved membrane hydrophilicity, which result in reduced membrane fouling.

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