Improvement of Permeation Performance of Polyethersulfone (PES) Ultrafiltration Membranes via Addition of Tween-20

Mohammad Amirilargani, Ehsan Saljoughi, Toraj Mohammadi

Research Centre for Membrane Separation Processes, Department of Chemical Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran

Received 28 January 2009; accepted 18 May 2009
DOI 10.1002/app.30814
Published online 8 September 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, effects of Tween-20 (polyoxyethylene sorbitan monolaurate) as a variable surfactant additive on morphology, permeation performance and antifouling properties of asymmetric polyethersulfone (PES) membranes were investigated. The membranes prepared from PES/polyethylene glycol (PEG)/*N*,*N*-dimethylformamide (DMF) system via phase inversion induced by immersion precipitation in water coagulation bath. The membranes performances were evaluated using ultrafiltration (UF) experiments. The scanning electron microscope and atomic force microscopy analysis were performed to investigate the membrane morphology. The obtained results indicate that by increasing the concentration of Tween-20, the membrane morphology changes slowly from thin finger-like structure with spongy structure to long and wide finger-like structure with some macrovoids. Addition of surfactant to the casting solution increases the porosity of the membrane sublayer. It was found out that the rejection ratio of Bovine serum albumin (BSA) decreases, while the flux recovery ratio remarkably increases and the degree of irreversible fouling decreases.
 J Appl Polym Sci 115: 504–513, 2010

Key words: Polyethersulfone membrane; phase inversion; Tween-20; surfactant; morphology; Antifouling; membrane performance

INTRODUCTION

Generally, polyethersulfone (PES) is widely used for preparation of microfiltration (MF), ultrafiltration (UF), and gas separation (GS) membranes. It has been suggested as a polymeric material for preparation of phase inversion membranes. Because it has favorable characteristics such as wide temperature limits, wide pH tolerances, fairly good chlorine resistance, wide range of pore sizes available for UF and MF applications ranging from 10 Å to 0.2 μm and good chemical resistance to aliphatic hydrocarbons, alcohols, and acids.[1,2] UF, as a developing and powerful pressure-driven separation technology, is often used to concentrate or fractionate protein solutions. However, adsorption and deposition of biomacromolecules on membrane surfaces and/or pore walls (the so-called membrane fouling), often cause severe flux decline, substantial energy consumption and significant operational cost. Applications of UF are seriously limited by the membrane fouling. In recent years, many researchers have revealed that increasing the hydrophilicity of the membrane surfaces and pore walls can remarkably reduce or suppress the membrane fouling.[3–7] It was found that in initial stage of UF, protein-membrane interactions hava major influence on the membrane fouling, while in subsequent stage, protein–protein interactions govern the membrane fouling.[8,9] A general method to suppress the membrane fouling, especially irreversible fouling is to inhibit protein-adsorption on the membrane surface by increasing hydrophilicity of the membrane surface.[10–12] Accordingly, hydrophilic molecules, such as poly(ethylene glycol) (PEG) and zwitterionic molecules, have been widely used to modify UF membranes.[13,14] Generation of protein-adsorption-resistant surfaces has attracted significant efforts for design and manipulation of materials structure and composition.[15–17] Many investigations have demonstrated that increasing membrane surface hydrophilicity could effectively inhibit membrane fouling. Therefore, various methods including blending, coating, adsorption, chemical-grafting, and radiation-induced grafting have been invented to modify membrane surface using hydrophilic modifiers.[18–20] However, these methods suffer the drawbacks of requiring additional complicated steps and offering random control over the resulting surface structure. A promising *in situ* membrane surface modification approach is to appropriately manipulate spontaneous migration

Correspondence to: T. Mohammadi (torajmohammadi@iust.ac.ir).

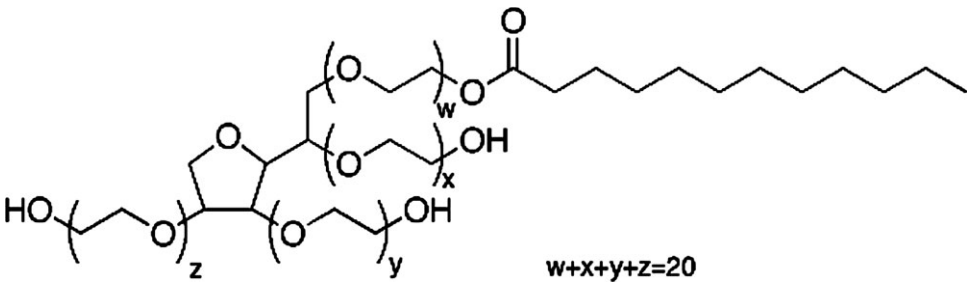

Figure 1 Tween-20 molecule structure.

of amphiphilic copolymers from membrane casting solutions onto the membrane surfaces.[21–24] Addition of surfactant additives to the casting solutions can influence morphology and performance of the membranes. Some researchers studied the effects of surfactant additives with hydrophilic properties on the membrane morphology and performance. Rahman et al.[25] studied the effects of Tetronic-1307 as a surfactant additive on morphology and performance of PES porous hollow-fiber membranes and found that increasing the Tetronic 1307 content increases hydrophilicity of the membranes. Alsari et al.[26] used sodium dodecyl sulphate as a surfactant additive as gelation media on formation of PES membranes. The effects of Triton X-100 as a nonionic surfactant additive were also investigated by Rahimpour et al.[27] There is no previous published article regarding addition of Tween series surfactants as hydrophilic additives for improvement of permeation and anti fouling properties of the PES membranes. In this work, Tween-20 as a hydrophilic surfactant additive was selected to blend with PES in the membrane preparation process. The effects of Tween-20 on morphology and fouling-resistant ability of the PES membranes were investigated in details.

EXPERIMENTAL

Materials

Polyethersulfone (PES Ultrason E6020P with M_W = 58,000 Da) supplied by BASF was used as polymer for preparation of the membrane casting solution. These polymer flakes absorb moisture very rapidly. Therefore, the flakes were dried for more than 12 h at 100–120°C prior to the process. *N,N*-dimethylformamide (DMF) was used as solvent from Merck. Polyethylene glycol (PEG, reagent grade, M_W = 400 Da) supplied by Merck were used as a pore former polymeric additive in the casting solution. Tween-20 (Polyoxyethylene sorbitan monolaurate, HLB = 16.7) as a surfactant additive supplied by merck was used as a nonionic surfactant additive in the casting solution. The chemical structure of Tween-20 is shown in Figure 1. De-ionized water was used as the main non-solvent in the coagulation bath. Bovine serum albumin (BSA, M_W = 67,000 g/mol) obtained from Merck (Germany) and was used as protein in preparation of the model solution.

Preparation of the membranes

Asymmetric flat sheet PES membranes were prepared by the phase inversion method. To the homogeneous solution of PES in DMF, PEG 400 as invariable polymeric additive and Tween-20 as variable surfactant additive were added and mixed by stirring for 8 h at room temperature. In all experiments, PEG was added to the polymeric solution by 5 wt %. The stirring was carried out at 200 rpm. When necessary, an ultrasonic bath (KUDOS SK3310HP, China) was employed to help free up of the air bubbles entrapped in the polymeric solution. The prepared homogeneous solutions were cast using a film applicator to 250 μm clearance gap on a glass plate substrate. It was then moved to the distilled water coagulation bath at room temperature for immersion precipitation and kept for 24 h. This was done to ensure complete removal or evaporation of residual solvent from the membranes. Finally, the membranes were dried by placing between two sheets of filter paper for 24 h at room temperature. Composition of the casting solutions is shown in Table I.

Characterization of the membranes

Scanning electron microscopy (SEM)

Structures of the prepared membranes were examined by scanning electron microscope (SEM). The

TABLE I
Compositions of the PES Casting Solutions

Membrane	PES (wt %)	PEG 400 (wt %)	DMF (wt %)	Tween-20 (wt %)
T0	17	5	78	–
T1	17	5	77	1
T2	17	5	76	2
T3	17	5	75	3
T4	17	5	74	4

samples were frozen in liquid nitrogen and then fractured. They were then sputter coated with gold before being viewed with SEM (JXA-840, JEOL, Japan).

Determination of mean pore size, surface porosity and membrane roughness using AFM

AFM DualScopeTM scanning probe-optical microscope (DME model C-21, Denmark) was employed to analyze surface morphology of the membranes. Small squares of the prepared membranes were cut and glued on a glass substrate. The membranes surfaces were examined in a scan size of 1 μm × 1 μm. Pore sizes of the membranes were calculated from height profile of AFM images using SPM software. Size of each randomly chosen pore was obtained from information related to the height profile and the pore entrance. The measured pore sizes were arranged in ascending order, and the corresponding median ranks (50%), χ, were calculated using the following equation[28,29]:

$$\chi = \frac{j - 0.3}{n + 0.4} \tag{1}$$

where j is the order number of pore sorted in ascending order and n is the total number of measured pores. The medians were plotted against the measured pores on log-normal probability paper. This graph produces a straight line if pore sizes have a log normal distribution. From this plot, mean pore size (μ_p) and geometric standard deviation (σ_p) can be obtained. The mean pore size is equivalent to 50% of the cumulative number of pores and the geometric standard deviation corresponds to a ratio between 84.13% and 50% of the cumulative number of pores.[28,29] The pore size distribution of membranes can be obtained from the calculated values of mean pore size and geometric standard deviation using the following equation[28,29]:

$$\frac{df(d_p)}{d(d_P)} = \frac{1}{d_P \ln \sigma_P (2\pi)^{0.5}} \exp\left[\frac{(\ln d_P - \ln \mu_P)^2}{2(\ln \sigma_P)^2}\right] \tag{2}$$

The surface porosity of membranes (S_p) is defined as ratio of the area of pores to the total surface area and can be obtained as[28,29]:

$$S_P = \left(\frac{n\pi}{4} \sum_{d_{\min}}^{d_{\max}} f_i d_i^2\right) \times 100 \tag{3}$$

where n is the total number of pores and f_i is the fraction of pores with diameter d_i.

Water content

Water content is considered to be an important characterization parameter as it indirectly indicates degree of hydrophilicity or hydrophobicity of the prepared membranes and also it is related to the porosity of the prepared membranes.[30] The membranes were soaked in distilled water for 24 h and weighed after mopping with blotting papers. The dry weights were determined after the wet samples were placed in an oven at 80°C for 24 h. From these two values, the percent of water content was obtained using the following equation[31]:

$$\text{Water content } (\%) = \frac{(Q_0 - Q_1)}{Q_0} \times 100 \tag{4}$$

where Q_0 is the weight of wet membrane (g) and Q_1 is the weight of dry membrane (g).

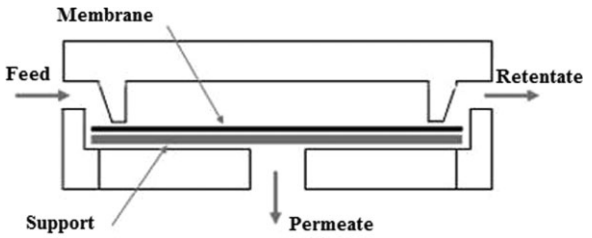

Figure 2 Schematic view of the experimental module.

Permeation experiment

Cross flow UF system

Performance of the prepared membranes was characterized using a cross flow UF system. This laboratory scale system consisted of a reservoir, a pump, valves, pressure regulators and a membrane cell. A flat sheet membrane module made from stainless steel was used in all the experiments. Effective area of the membrane in the module was 25 cm^2. The channel height of the module on upstream side was 1.5 mm. Schematic representations of the module and the cross-flow set-up are shown in Figures 2 and 3, respectively. As seen, retentate was re-circulated to the reservoir and permeate was collected and then weighed.

UF experiments

The prepared membranes were initially compacted before evaluation in the separation experiments. They were cut into the desired size needed for sealing the cell and pressurized with distilled water at a transmembrane pressure (TMP) of 220 kPa for 1 h. Membrane permeability was then determined by allowing de-ionized water to pass through the compacted membrane. Pure water flux (PWF) through the membranes was measured under steady state condition. The experiments were carried out using a cross flow UF system at a TMP of 100 kPa. All the experiments were conducted at room temperature.

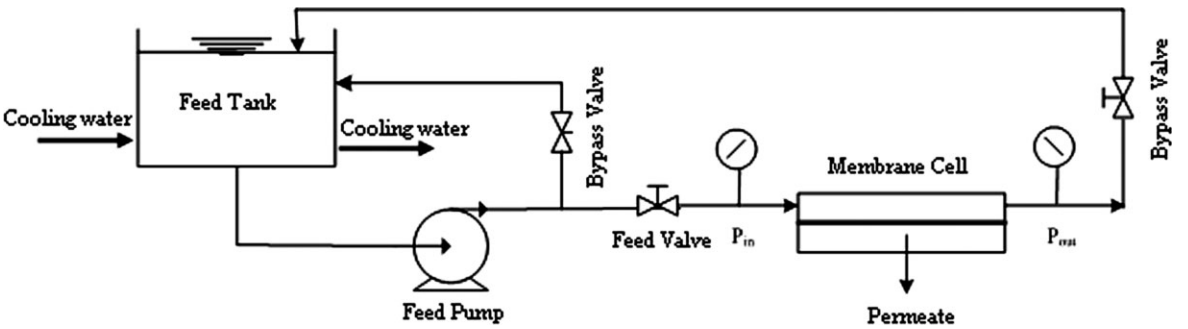

Figure 3 Schematic diagram of the experimental set-up.

PWF was calculated as follows:

$$J_{W1} = \frac{V}{A\Delta T} \tag{5}$$

where J_{W1} is the PWF (L/m^{2}h); V is the volume of permeate (L); A is the membrane area (m^2); and ΔT is the permeation time (h).

After that UF experiments were carried out using the protein solution. The protein, BSA, was dissolved in de-ionized water and its concentration was kept constant at 1 g/L for all the experiments. In all the experiments, the protein solution was adjusted at a pH value of 7.2 using buffer solutions. The protein solution flux (J_P) was calculated using eq. (5). Rejection of BSA was calculated using the following equation:

$$R(\%) = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100 \tag{6}$$

where, C_p is protein concentration in the permeate stream and C_f is protein concentration in the feed stream. Samples from the permeate and the retentate were taken in order to determine their protein concentrations using UV spectrophotometry (Shimadzu® UVmini-1240) at 280 nm.[4,14] After UF of the protein solution, the membranes were washed with de-ionized water for 30 min and PWF of the cleaned membranes, J_{W2}, was measured. To evaluate the fouling-resistant ability of membranes, flux recovery ratio (FRR) was calculated using the following expression[32]:

$$\mathrm{FRR}(\%) = \left(\frac{J_{W2}}{J_{W1}}\right) \times 100 \tag{7}$$

To analyze the fouling phenomena in details, several ratios were defined to describe the fouling-resistant ability of the PES membranes. The first ratio was defined as r_t, was calculated using the following equation[32]:

$$r_t = 1 - \frac{J_P}{J_{W1}} \tag{8}$$

which describes the degree of total flux loss caused by total fouling. r_t and r_{ir} were also defined to distinguish flux reduction due to reversible fouling and irreversible fouling. r_r and r_{ir} were calculated using the following equations[32]:

$$r_r = \frac{J_{W2} - J_P}{J_{W1}} \tag{9}$$

$$r_{ir} = \frac{J_{W1} - J_{W2}}{J_{W1}} \tag{10}$$

Obviously, r_t was the sum of r_{ir} and r_r:

$$r_t = r_r + r_{ir}$$

RESULTS AND DISCUSSIONS

For a hydrophilic coagulant, hydrophilic surfactants are able to improve the macrovoids formation and hydrophilicity of the membranes. However, lipophilic surfactants do not have these properties. On the other hand for a lipophilic coagulant, lipophilic surfactants are more effective on changing the membrane structure.[27,33] In this work, the effects of concentration of Tween-20 as a nonionic surfactant on morphology, permeation properties and fouling properties of the PES membranes were investigated.

Effects of Tween-20 as hydrophilic surfactant additive on morphology of the PES membranes

Microscopic studies using SEM images were carried out to reveal qualitative information regarding cross-sectional morphology of the prepared membranes. SEM cross-sectional images of the prepared PES membranes using different concentration of Tween-20 as surfactant additive are presented in Figure 4. The SEM images exhibit the typical asymmetric finger-like structure by spongy structure in the sublayer for the membrane prepared without Tween-20 [Fig. 4(a)]. Asymmetric structure of the membranes consists of a dense top layer, a porous sublayer that

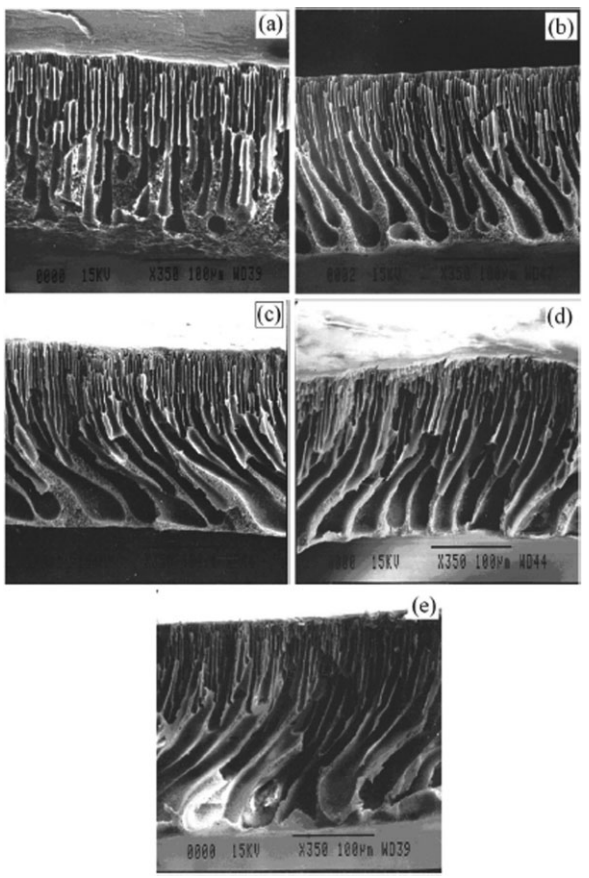

Figure 4 SEM cross-sectional images of the PES membranes prepared with different concentration of tween-20: (a) 0 wt %, (b) 1 wt %, (c) 2 wt %, (d) 3 wt %, and (e) 4 wt %.

is occupied by closed cell within polymer matrix, and finger-like pores. Strathmann et al.[34] investigated that highly porous membranes can prepared when the coagulant (NS) enters the nascent membrane faster than the solvent escapes, while dense membranes can be prepared when the solvent escapes faster than the coagulant (NS) enters. The SEM images indicate that macrovoids are formed in the sublayer of the membranes prepared with addition of little amount of Tween-20 to the casting solution [Fig. 4(b,c)]. This phenomenon can be explained by the miscibility between the added surfactant and the coagulant. However, the low solubility of Tween-20 as a hydrophilic surfactant additive in a solvent such as DMF may be introduced as a factor for changing the membrane morphology and performance. The miscibility between the added surfactant and the coagulant plays an important role in the formation process of macrovoids.[33] The macrovoids and finger-like pores in the sublayer can be induced or suppressed by addition of appropriate surfactants, depending on their miscibility with the coagulant. A formation mechanism of macrovoids was proposed by Smolders et al.[35] They said that the instantaneous demixing, resulting from the contact between the casting solution and the coagulant, can generate nucleated droplets of the polymer lean phase in the casting polymer solution, and these nuclei are responsible for the initiation of macrovoids. Addition of the surfactants that have high miscibility with the coagulant may be able to enhance the formation of finger-like pores and macrovoids. On the other hand, addition of the surfactants with low miscibility with the coagulant suppresses the macrovoids formation. The SEM cross-sectional images of the membranes prepared with high concentrations (3 and 4 wt %) of Tween-20 as a surfactant additive [Fig. 4(d,e)] indicate that addition of large amount of Tween-20 to the casting solution can incite macrovoids formation. As observed from SEM images, there are big macrovoids in the sublayer structure of these membranes.

Determination of membrane surface morphology, mean pore size and surface porosity using AFM

Two and three dimensional surface AFM images of the membranes prepared using 0 and 2 wt % of Tween-20 are presented in Figure 5. In these images, the brightest area presents the highest point of the membrane surface and the dark regions indicate valleys or the membrane pores. As observed in Figure 5(a), the PES membrane prepared without surfactant exhibits relatively large pores in the selected surface area and the formation of nodules on the membrane surface is approximately reduced. The PES membrane prepared using 2 wt % of Tween-20 demonstrates similar surface morphology with a rough and mottled surface consisting of well-defined depression pores and channels as observed in Figure 5(b). By comparison of the images in Figure 5(a,b), it can be observed that the size of surface pores decreases by addition of 2 wt % of Tween-20 to the casting solution. For quantitative analysis, average pore size of the membranes surfaces were obtained from AFM images using DME SPM software (version 2.1.1.2). The size of 30 pores in 1 μm × 1 μm area of the membrane surfaces were measured from height profile of two-dimensional AFM images using SPM software.[28] Height profiles at 10 randomly chosen lines were selected from AFM micrographs. The 30 measured pore sizes were drawn against the median ranks on log-normal probability paper (Fig. 6). Curves with very high correlation coefficients (R^2 >0.94) through the obtained data for both the membranes indicate a log-normal distribution for the pore sizes. The mean pore size (μ_p) and the standard geometric deviation (σ_p) for the membranes were obtained from data plotted in Figure 6. The results are presented in Table II. Pore size distribution of the membranes

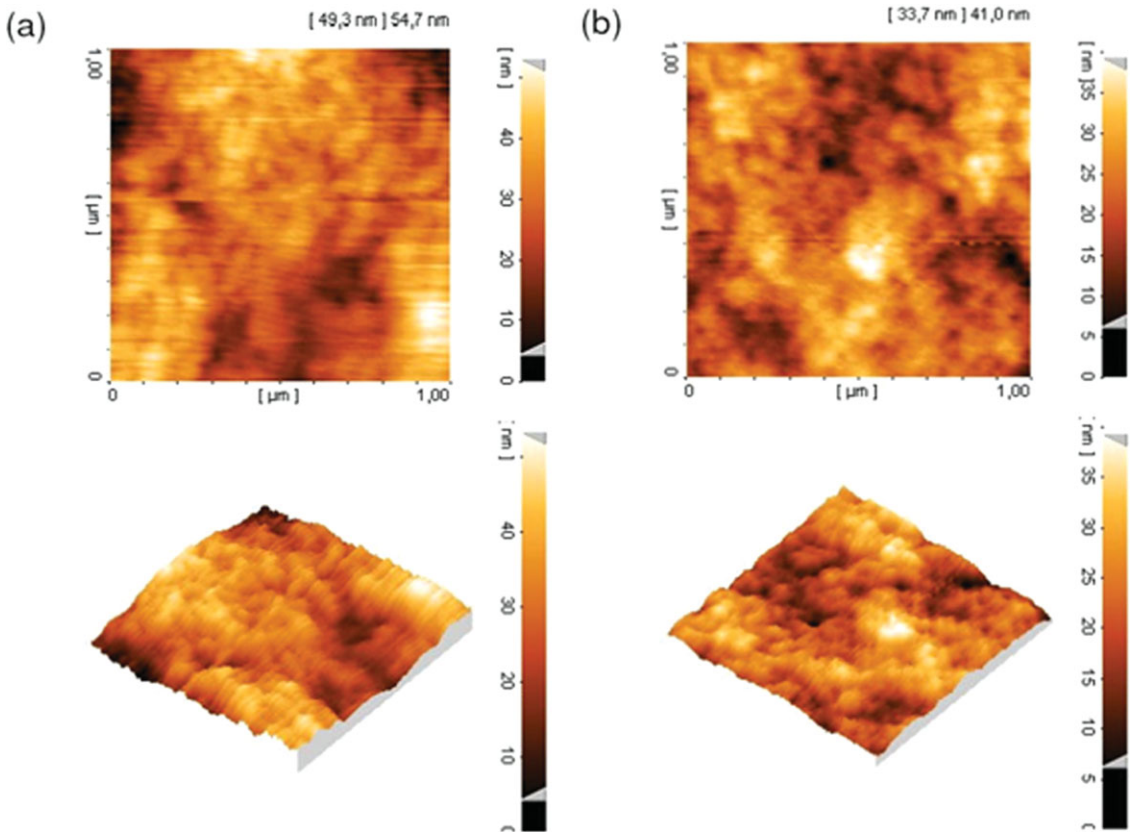

Figure 5 Two and three dimensional AFM surface images of the PES membranes (a) T0 and (b) T2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

were generated on the basis of eq. (2) using the mean pore size (μ_p) and the standard geometric deviation (σ_p) measured using Figure 6. The results are presented in Figure 7. As can be observed there is a change in pore size distribution for the membranes. The pore size distribution shifted to the left by addition of Tween-20 as a hydrophilic surfactant additive to the casting solution. Surface porosity of the membranes was obtained using eq. (3). The calculated results are shown in Table II. The obtained data indicate that surface porosity of the membranes increase by addition of 2 wt % of Tween-20 to the casting solution.

Permeation properties of the PES membranes

UF experiments were carried out to study permeability and antifouling properties of the PES membranes. The obtained results were presented in Table III. As observed, PWF of PES membranes increases by increasing Tween-20 concentration. For example, PWF of T0 membrane prepared with no Tween-20 in the casting solution is 36.9 L/m^{2}h and increases to 152.8 L/m^{2}h by addition 4 wt % of Tween-20 to the casting solution (T4 membrane). Increasing PWF of the PES membranes prepared via addition of Tween-20 as surfactant additive to the casting solution may be due to the combined effects of porosity and hydrophilicity of the PES membranes. Composition (concentration, solvent, additives) of the casting solution was found to be one of the important key factors influencing on morphology and performance of the prepared membranes.[36,37]

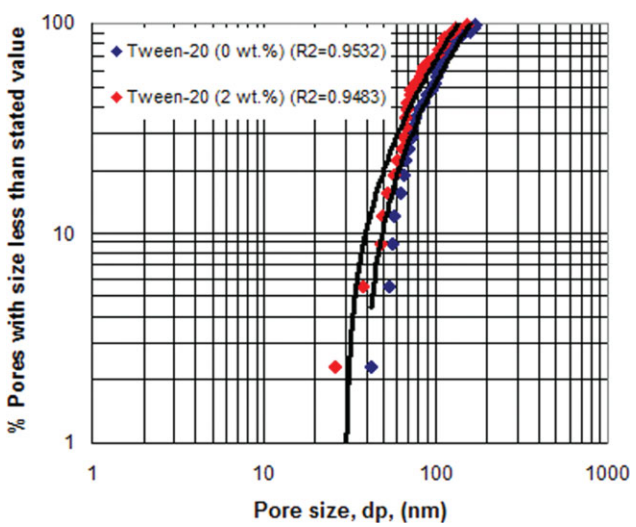

Figure 6 Pore size distribution of the prepared membranes obtained from AFM photos on log-normal probability paper. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Mean Pore Size, Standard Geometric Deviation and Surface Porosity Calculated from AFM Images

Tween-20 (wt %)	Mean pore size (μ_p nm)	Standard geometric deviation (σ_p)	Surface porosity (%)
0	96.1	1.32	29.60
2	73.2	1.53	35.31

The effect of Tween-20 addition to the casting solution is presented schematically in Figure 8. Tween-20 is amphiphilic (i.e. with hydrophilic head and hydrophobic tail), water (nonsolvent) and DMF (solvent) are hydrophilic, therefore a layer of Tween-20 molecules is formed at solvent (DMF) and nonsolvent (water) phase interface and this increases the rate of nonsolvent-solvent exchange. When solvent in the casting solution and nonsolvent in the coagulation bath first contact with each other during the membrane preparation process, most of the nonsolvent flows rapidly into the casting solution, leading to the formation of more nuclei and the growth of highly concentrated polymer in the porous sublayer simultaneously.[38] On the other hand, DMF is hydrophilic and PES is hydrophobic. Tween-20 molecules and PES are likely to form a micelle-like complex in the casting solution. Formation of this complex reduces interaction between the polymer chains. Both phenomena result in a delay in coagulation of the polymer in the presence of Tween-20. Consequently, the growth of skin layer is diminished and formation of finger-like pores in the support is improved.[27] The formation of Tween-20 micelles enables flexible adjustment of the skin layer pore size Since addition of nonsolvent varies the casting composition, the membrane casting system crosses the binodal boundary into the unstable zone, and the first nucleus of the Tween-20 micelle performs formation of the pores in the skin layer. The micelles of Tween-20 are trapped in the skin layer during the coagulation process. The repulsive interaction between Tween-20 micelles and PES looses the skin layers of the formed membranes.[38]

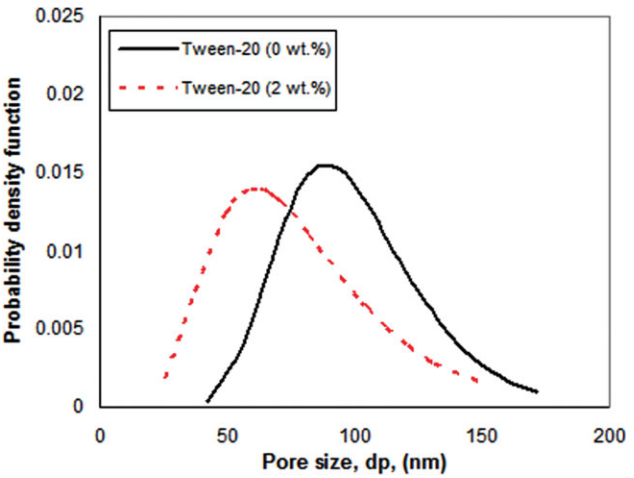

Figure 7 Pore size distribution of the prepared membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of TMP on PWF of the PES membranes

The effects different concentrations of Tween-20 on PWF at various TMPs is presented in Figure 9. As observed, PWF through all the membranes within a TMP range of 0–140 kPa increases almost linearly with pressure. This is because increasing the operating pressure increases the required driving force for water permeation in UF process.[39] Also, PWF through all the membranes increases with increasing Tween-20 concentration at a particular pressure. For example, at 120 kPa, PWF increases from 43.2 to 189.3 L/m^{2}h when Tween-20 concentration in the casting solution increases from 0 to 4 wt %. The slope of these straight lines can be used as an indication of the hydraulic resistance during UF. The membrane with higher slope shows less resistance. In the other words, the higher slope, the lower resistance.[40] Due to the combined effects of increasing hydrophilicity and porosity of the membrane surface, increasing Tween-20 concentration in the casting solution increases the slope of straight lines.

Fouling-resistant ability of the PES membranes

Under constant TMP, the effects of membrane fouling and concentration polarization are usually

TABLE III
Permeation and Antifouling Properties of the PES Membranes (at TMP = 100 kPa and pH = 7.2)

Membrane	J_{W1} (L/m^{2}h)	J_P (L/m^{2}h)	J_{W2} (L/m^{2}h)	Rejection (%)	r_t	r_r	r_{ir}	FRR (%)
T0	36.9	13.8	20.2	96.4	0.63	0.17	0.46	54.7
T1	59.4	24.4	37.8	94.8	0.59	0.23	0.36	63.6
T2	99.2	42.2	65.9	93.3	0.57	0.24	0.33	66.4
T3	121.8	69.4	99.4	92.1	0.43	0.25	0.18	81.6
T4	152.8	88.6	129.2	90.8	0.42	0.27	0.15	84.5

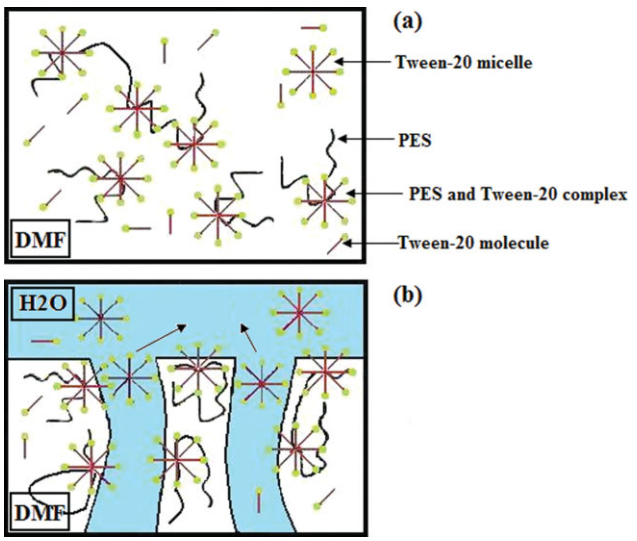

Figure 8 Presence of Tween-20 in the membrane preparation process; (a) status of Tween-20 in the casting solution, (b) status of the cast film in the water coagulation bath. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed by a considerable decline in permeation flux with time. PWF values of the prepared membranes, before and after UF of the BSA solution are presented in Figure 10. As observed, PWF of all the membrane decreases after UF of the BSA solution. This reduction is less for the membranes prepared with more concentration of Tween-20 in the casting solution. For example, PWF decreases from 36.9 to 20.9 L/m^{2}h for the membrane prepared with no Tween-20 in the casting solution (T0 membrane), while decreases from 152.8 to 129.2 L/m^{2}h for the membrane prepared with 4 wt % Tween-20 in the casting solution (T4 membrane). Protein solution flux (J_P) of the PES membranes is presented in Figure 11. As observed, J_P increases with increasing

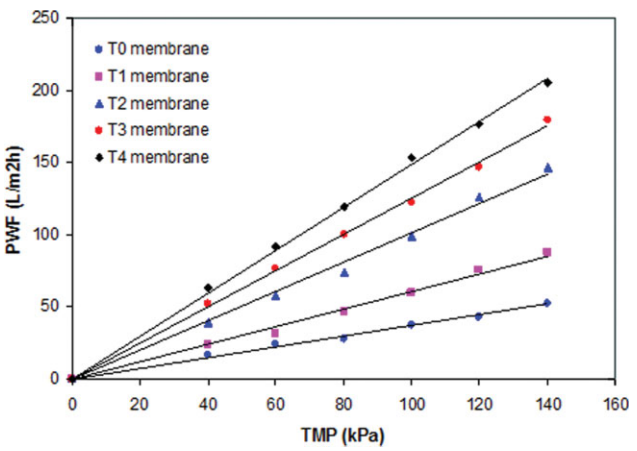

Figure 9 Effect of TMP on PWF of the PES membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

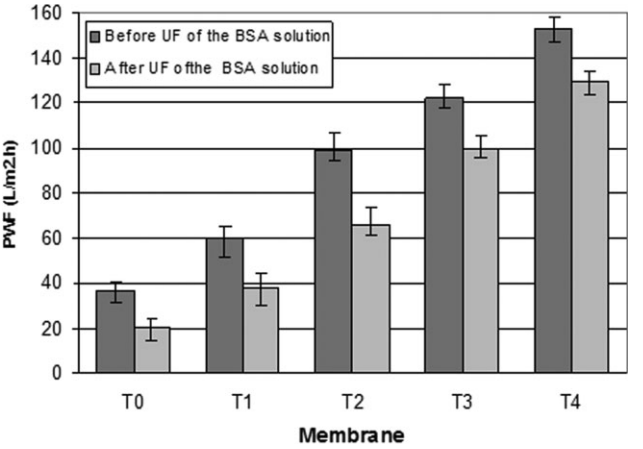

Figure 10 PWF of the PES membranes before and after UF of the BSA solution.

Tween-20 concentration in the casting solution. The effect of Tween-20 concentration on the BSA rejection through the membranes was presented in Table III. As observed, BSA rejection decreases by increasing Tween-20 concentration. For example, BSA rejection decreases from 96.4 to 90.8% when the Tween-20 concentration increases from 0 to 4 wt %. This BSA rejection reduction is due to the macrovoids formation in the membrane structure by increasing the Tween- 20 concentration (Fig. 4). FRR was introduced to evaluate the recycling property of the PES membranes. The FRR values of the membranes were calculated and presented in Table III. FRR values of all of the PES membranes were higher than 54.7%. As observed in Table III, FRR increases by increasing Tween-20 concentration and reaches to a maximum value of 84%, for the membrane

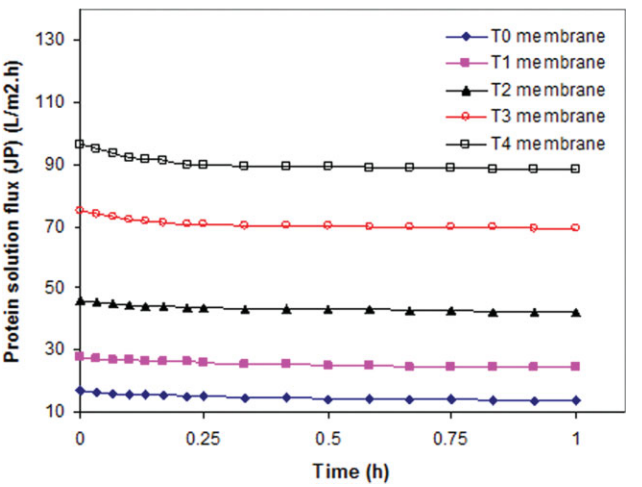

Figure 11 Time-dependent protein solution flux of the PES membranes during UF of BSA solution. UF was carried out at a temperature of 25°C and a TMP of 100 kPa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

prepared with 4 wt % Tween-20 in the casting solution (T4 membrane). By addition of Tween-20 as a nonionic surfactant additive with long polyether chains as hydrophilic groups to the casting solution, most of the protein fouling becomes reversible due to the introduction of hydrophilic chains at the membrane surface.[41]

Recycling of PES membranes

The excellent flux recovery property of PES membranes prepared with Tween-20 as a hydrophilic surfactant additive indicated that the prepared membranes could be reused for several runs. To evaluate the recycling potential of PES membranes prepared with 0, 2, and 4 wt % Tween-20, three repetitive UF runs were carried out, and the results presented in Figure 12. As observed, PWF of the PES membrane prepared with no Tween-20 in the casting solution (T0 membrane), decreased to nearly zero after three runs of UF. However, PWF of the membranes prepared with 2 and 4 wt % Tween-20 in the casting solution (T2 and T4 membranes), decreased to 40.08 and 170.2 L/m2h after three runs of UF. These results revealed that the recycling potential of the PES membranes prepared with Tween-20 improved due to incorporation of hydrophilic properties and formation of macrovoids in the PES membrane structure.

Effect of Tween-20 concentration on water content of the PES membranes

Water content of the prepared membranes calculated using eq. (4) is presented in Figure 13. It was found out that addition of Tween-20 to the casting solution enhances water content of all the membranes. For example, water content of the membranes increases from 68.5 to 76.3%, when Tween-20 concentration in the casting solution increases from 0 to 4 wt %.

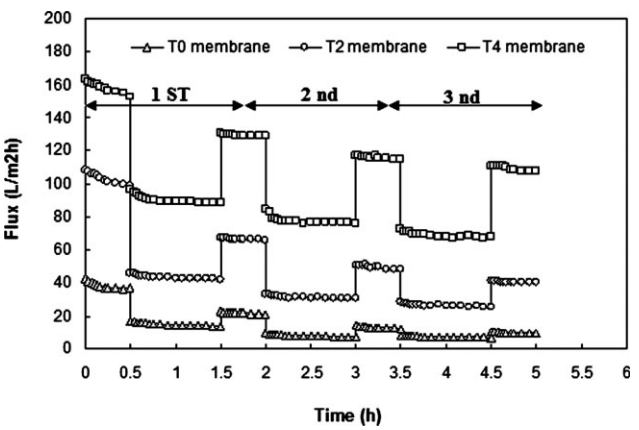

Figure 12 Flux variation of the PES membranes during three runs of UF (TMP = 100 kPa).

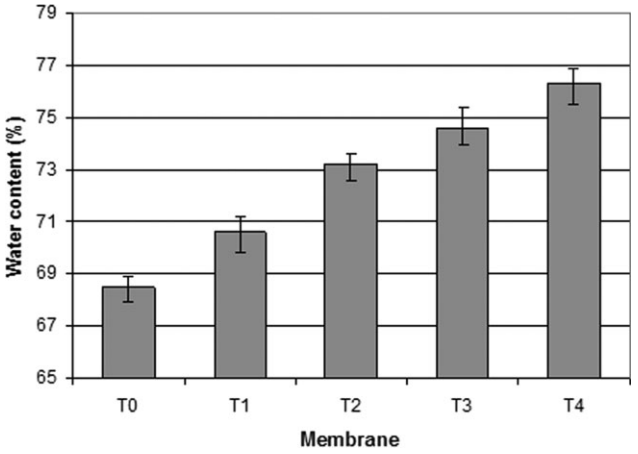

Figure 13 Effect of Tween-20 concentration on water content of the PES membranes.

Addition of Tween-20 as a hydrophilic surfactant additive to the casting solution may favor formation of larger pores in the support layer of the prepared membranes, and as a result, the membranes become more porous (Fig. 4). When the additive concentration increases, repulsive forces between the polymer segments along with leachability of the additive enhance and this favors formation of macrovoids due to occurrence of more number of larger pores.[31] The pores on the surface as well as the cavities in the sublayer are responsible for accommodating water molecules in the membranes.[42]

CONCLUSIONS

The effects of Tween-20 concentration as a hydrophilic surfactant additive in PES/DMF casting solutions on the fundamental characteristics of the membranes such as cross-sectional and surface morphology, PWF, water content, protein solution flux and protein rejection were investigated. All the membranes have asymmetric structure as observed in the SEM cross-sectional images. By increasing the concentration of Tween-20 in the casting solution, the membrane morphology changed slowly from thin finger-like structure with spongy structure in the sublayer to long and wide finger-like structure with some macrovoids in the sublayer. Surface analysis of the membranes showed that surface porosity of the PES membranes prepared with Tween-20 in the casting solution was higher, while their mean pore size was lower compared with the membrane prepared with no Tween-20 in the casting solution. Accordingly, irreversible fouling and total fouling of the PES membranes remarkably decreased. PWF could be flexibly tuned by varying Tween-20 content in the casting solution. Furthermore, the excellent flux recovery rendered the PES membranes with their desirable recycling potential were observed.

Finally, it was concluded that pore size and pore size distribution and even porosity of the PES membranes can be controlled by addition of Tween-20 as a surfactant additive to the casting solution in the immersion precipitation process.

References

1. Zhen-Liang, X. U.; Alsalhy Qusay, F. J Membr Sci 2004, 233, 101.
2. Shi, Q.; Su, Y.; Zhu, S.; Li, C.; Zhao, Y.; Jiang, Z. J Membr Sci 2007, 303, 204.
3. Liu, Z. M.; Xu, Z. K.; Wan, L. S.; Wu, J.; Ulbricht, M. J Membr Sci 2005, 249, 21.
4. Reddy, A. V. R.; Mohan, D. J.; Bhattacharya, A.; Shah, V. J.; Ghosh, P. K. J Membr Sci 2003, 214, 211.
5. Taniguchi, M.; Belfort, G. J Membr Sci 2004, 231, 147.
6. Pieracci, J.; Crivello, J. V.; Belfort, G. J Membr Sci 1999, 156, 223.
7. Chen, H.; Belfort, G. J Appl Polym Sci 1999, 72, 1699.
8. Saksena, S.; Zydney, A. L. J Membr Sci 1997, 125, 93.
9. Bae, T. H.; Tak, T. M. J Membr Sci 2005, 264, 151.
10. Taniguchi, M.; Pieracci, J.; Samsonoff, W. A.; Belfort, G. Chem Mater 2003, 15, 3805.
11. Hasegawa, T.; Iwasaki, Y.; Ishihara, K. Biomaterials 2001, 22, 243.
12. Wang, Y.; Su, Y.; Sun, Q.; Ma, X.; Ma, X.; Jiang, Z. J Membr Sci 2006, 282, 44.
13. Kang, S.; Asatekin, A.; Mayes, A. M.; Elimelech, M. J Membr Sci 2007, 296, 42.
14. Sun, Q.; Su, Y.; Ma, X.; Wang, Y.; Jiang, Z. J Membr Sci 2006, 285, 299.
15. Kenausis, G.; Vo1ro1s, J.; Elbert, D.; Huang, N. J Phys Chem B 2000, 104, 3298.
16. Huang, N.; Michel, R.; Voros, J.; Textor, M.; Hofer, R. Langmuir 2001, 17, 489.
17. Herrwerth, S.; Eck, W.; Reinhardt, S.; Grunze, M. J Am Chem Soc 2003, 125, 9359.
18. Roux, S.; Jacobs, E.; Van Reenen, A.; Morkel, C.; Meincken, M. J Membr Sci 2006, 276, 8.
19. Meincken, M.; Roux, S.; Jacobs, E. Appl Surf Sci 2005, 252, 1772.
20. Ulbricht, M. Polymer 2006, 47, 2217.
21. Wang, Y. Q.; Su, Y. L.; Suna, Q.; Ma, X. L.; Jiang, Z. Y. J Membr Sci 2006, 286, 228.
22. Hancock, L.; Fagan, S.; Ziolo, M. Biomaterials 2000, 21, 725.
23. Yong, K.; Woong, A.; Jae, K.; Young, K. Biomaterials 2005, 26, 2867.
24. Park, J.; Acar, M.; Akthakul, A.; Kuhlman, W.; Mayes, A. Biomaterials 2006, 27, 856.
25. Rahman, N. A.; Sotani, T.; Matsuyama, H. J Appl Polym Sci 2008, 108, 3411.
26. Alsari, A. M.; Khulbe, K. C.; Matsuura, T. J Membr Sci 2001, 188, 279.
27. Rahimpour, A.; Madaeni, S. S.; Mansourpanah, Y. J Membr Sci 2007, 296, 110.
28. Singh, S.; Khulbe, K. C.; Matsuura, T.; Ramamurthy, P. J Membr Sci 1998, 142, 111.
29. Khayet, M.; Matsuura, T. J Membr Sci 2003, 158, 57.
30. Arthanareeswaran, G.; Latha, C. S.; Mohan, D.; Raajenthiren, M.; Srinivasan, K. Sep Sci Technol 2006, 41, 2895.
31. Sivakumar, M.; Mohan, D. R.; Rangarajan, R. J Membr Sci 2006, 268, 208.
32. Wang, Y.; Su, Y.-L.; Sun, X.-L.; Jiang, Z.-Y. J Membr Sci 2006, 283, 440.
33. Wang, D. M.; Lin, F. C.; Wu, T. T.; Lai, J. Y. J Membr Sci 1998, 142, 191.
34. Strathmann, H.; Kock, K.; Amar, P.; Baker, R. W. Desalination 1975, 16, 179.
35. Smolders, C. A.; Reuvers, A. J.; Boom, R. M.; Wienk, I. M. J Membr Sci 1992, 73, 259.
36. Saljoughi, E.; Amirilargani, M.; Mohammadi, T. J Appl Polym Sci 2009, 111, 2537.
37. Amirilargani, M.; Mohammadi, T. Polym Adv Technol Accepted, Early view.
38. Zhao, W.; Su, Y.; Li, C.; Shi, Q.; Ning, X.; Jiang, Z. J Membr Sci 2008, 318, 405.
39. Arthanareeswaran, G.; Thanikaivelan, P.; Srinivasn, K.; Mohan, D.; Rajendran, M. Euro Polym J 2004, 40, 2153.
40. Wang, Y.; Su, Y.; Sun, Q.; Ma, X.; Ma, X.; Jiang, Z. J Membr Sci 2006, 282, 44.
41. Wang, M.; Wu, D.; Shen, Q. Anal Chim Acta 2004, 519, 73.
42. Chakrabarty, B.; Ghoshal, A. K.; Purkait, M. K. J Membr Sci 2008, 309, 209.