Preparation and Characterization of Nanoporous Polysulfone Membranes with High Hydrophilic Property Using Variation in CBT and Addition of Tetronic-1107 Surfactant

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ABSTRACT: Asymmetric polysulfone (PSF) membranes were prepared from PSF, Tetronic-1107, and 1-methyl-2-pyrrolidone (NMP) via immersion precipitation. Pure water was used as the gelation media. The effects of coagulation bath temperature (CBT) (0 and 25°C), and addition of Tetronic-1107 on the morphology, wettability, and pure water permeation flux (PWF) of the prepared membranes were studied by scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle measurements, and experimental set up. The contact angle measurements demonstrated that the hydrophilicities of the nanoporous PSF membranes were significantly enhanced by addition of a small amount of Tetronic-1107 surfactant in the casting solution, along with using the lower CBT. It was also found that addition of Tetronic-1107 in the casting solution along with increasing the CBT from 0 to 25°C incites formation of bigger pores on the top surface and results in formation of membranes with higher thickness and more porous structure in the sublayer. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Membranes have gained an important place in chemical technology and been used in a wide range of applications, such as the production of high-quality water, removal or recovery of toxic or valuable components from various industrial effluents, and applications in the food and pharmaceutical industries.[1]

Currently, polymers are still the main materials in membrane technology because of the advantages such as good flexibility, toughness, and separation properties. However, a limited chemical, mechanical and thermal resistance restricts their applied scale. In fact, all polymers can be used as barrier or membrane materials, but their chemical and physical properties differ so much that only a limited number are used in practice.[2,3]

Polysulfone is a polymer, with excellent thermal and electrical properties over a wide temperature range.[4] Amorphous phase of PSF provides flexibility while the crystalline phase provides the desired thermal stability.[5] Other desirable properties include high chemical and hydrolytic stability as well as good mechanical and film-forming properties.[4,6] Because of its durability to hot water, steam, and alcohol, and because it is not noxious, PSF is widely used in the manufacture of medical devices, prep-aration of membranes and is broadly applied in water purification, biochemistry separation, hemodialysis, Chinese traditional herb drugs extraction and concentration, etc.[4,7]

Despite of above advantages, PSF membrane has a tendency toward contamination due to its hydrophobicity, which can result in declining of flux and life of the membrane.[4] Consequently, several researchers have examined altering membrane surface properties using various methods such as UV induced graft polymerization,[8–11] chemical modification,[8] redox initiated grafting,[12] plasma modification,[13] and ion-beam irradiation.[14]

A promising *in situ* membrane surface modification approach is to appropriately manipulate spontaneous migration of amphiphilic materials from membrane casting solutions onto the membrane surfaces.[15–18] 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 property on the membrane morphology and performance.

Yamasaki et al.[19] and Alsari et al.[20] used sodium dodecyl sulfate as surfactant additive in the polysulfone casting solution for gas separation and as gelation media on the formation of
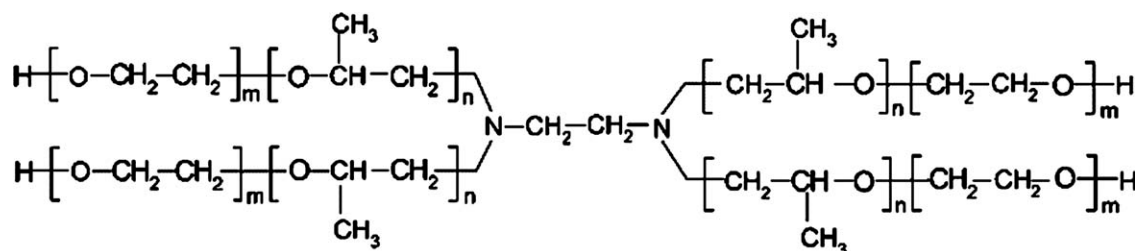
Figure 1. Tetronic molecule structure.

polyethersulfone membranes, respectively. The effect of addition of Tween 80 and Span 80 as surfactants in the casting solution on the formation of macrovoids in PMMA membranes was studied by Wang et al.[21] The effect of addition of Span 80 on the morphology and pervaporation performance of asymmetric polysulfone membranes was reported by Tsai et al.[22] The effect of Triton X-100 as a nonionic surfactant additive was also investigated by Rahimpour et al.[23]

There is no previous published article regarding the effects of addition of Tetronic-1107 surfactant as hydrophilic additives and variation in coagulation bath temperature for the improvement of permeation and wettability properties of the PSF membranes.

In this work, Tetronic-1107 as a hydrophilic surfactant additive was selected to blend with PSF in the membrane preparation process. The effects of Tetronic-1107 additive and variation in coagulation bath temperature on morphology, wettability, and pure water permeation flux (PWF) of the PSF membranes were investigated in details.

MATERIALS AND METHODS

Materials

Polysulfone (Ultrason S 6010), supplied by BASF, was used as polymer for preparation of the membrane casting solution. 1-methyl-2-pyrrolidone (NMP) with an analytical purity of 99.5% and distilled water were used as the solvent and the nonsolvent agents, respectively. Tetronic-1107 (Ethylenediamine tetrakis (propoxylate-block-ethoxylate) tetrol, HLB = 24), supplied by Aldrich, was used as a nonionic surfactant additive in the casting solution. The chemical structure of Tetronic is shown in Figure 1.

Preparation of the Membranes

Asymmetric flat sheet PSF membranes were prepared by phase inversion method. Tetronic-1107 was added to the homogeneous solution of PSF in NMP, and mixed by stirring for 12 h at room temperature. The stirring was carried out at 200 rpm. The prepared homogeneous solution was cast using a film applicator with 350 μm clearance gap on a glass plate substrate. It was then moved to the distilled water coagulation bath for immersion precipitation. After primarily phase separation and formation, the membrane was stored in water for 24 h to guarantee complete phase separation. This allowed the water soluble components in the membrane to be leached out. As the final stage, membrane was 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.

Membrane Characterization

Scanning Electron Microscopy. The membranes were snapped under liquid nitrogen to give a generally consistent and clean cut. The membranes were then sputter-coated with thin film of gold. The membranes were mounted on brass plates with double-sided adhesive tape in a lateral position. Cross-sectional images of the membranes were obtained with a CamScan SEM model MV2300 Microscope.

Atomic Force Microscopy. Atomic force microscopy was employed to analyze the surface morphology and roughness of membranes. The AFM apparatus was DualScope[TM] scanning probe-optical microscope (DME model C-21, Denmark). Small squares of the prepared membranes ($\sim$ 1 cm^2) were cut and glued on glass substrate. The membrane surfaces were examined in a scan size of 200 nm $\times$ 200 nm. 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 the information related to the height profile and pore entrance. The measured pore sizes were sorted in ascending order and median ranks (50%) were obtained from the following equation[24]:

$$\text{Median rank (or 50\% rank)} = \frac{k - 0.3}{n + 0.4} \qquad (1)$$

where k is the order number of the pore sorted in ascending order and n is the total number of measured pores. The medians were plotted against measured pores on log-normal probability paper. This graph will produce a straight line on log-normal probability paper if pore sizes have a log normal distribution. From this plot, the mean pore size (μ_p) and geometric standard deviation (σ_p) can be obtained. The mean pore

Table I. Composition of the PSF Casting Solutions and Coagulation Bath Temperature (CBT)

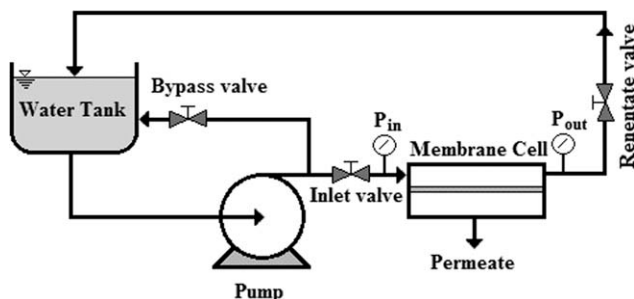| Membrane	PSF (wt %)	CBT (°C)	Tetronic-1107 (wt %)
M1	15	25	0
M2	15	25	2
M3	15	25	4
M4	15	25	6
M5	15	0	0
M6	15	0	2
M7	15	0	4
M8	15	0	6

Figure 2. Schematic diagram of membrane pilot.

size is equivalent to 50% of the cumulative number of pores and geometric standard deviation corresponds to the ratio between 84.13% and 50% of the cumulative number of pores.[19,20] 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:

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

Contact Angle. To evaluation of the membranes hydrophilicity, the contact angle between water and the membranes was directly measured using a contact angle measuring instrument [G10, KRUSS, Germany]. Deionized water was used as the probe liquid in all the measurements.

Pure Water Flux. A membrane pilot containing a disk membrane module made from stainless steel was used in the experiments. The effective membrane area in the module was 20 cm^2. The schematic representation of membrane pilot is shown in Figure 2. PWF experiments were conducted at a transmembrane pressure of 10 bar using the following equation:

$$\text{Flux} = \frac{Q}{A\Delta t} \qquad (3)$$

where Q is the quantity of permeate (l), A is the effective membrane area (m^2), and Δt is the sampling time (h).

RESULTS AND DISCUSSION

Morphological Studies of the Prepared Membranes
Membrane Formation Mechanism. Microscopic studies using SEM images were carried out to find out the qualitative information regarding the cross-sectional morphology of the prepared membranes. SEM images from the prepared membranes and trend of their thickness are illustrated in Figure 3.

Figure 3 exhibits a typical asymmetric structure and fully developed pores. Asymmetric structure of the membrane comprises a dense thin top layer and a porous sub-layer which is filled up by the closed cells within polymer matrix and finger like macrovoids. Using Figure 3, the effects of different concentrations of Tetronic-1107 as a hydrophilic additive and two different levels of CBT, 0 and 25°C, on the morphology and thickness of the PSF membranes can be studied. As observed from the SEM

images, increase in CBT from 0 to 25°C along with increase in Tetronic-1107 concentration from 0 to 6 wt % results in:

1. Greater formation of macrovoids and more porous structure (Figure 3)
2. Noticeable increase in the thickness of the prepared membranes (Figures 3 and 4)

An explanation for these observations requires an understanding of the membrane formation mechanism explained in our previous articles.[25–27] In brief, when the cast film is immersed into the distilled water bath, precipitation starts because of the low miscibility between the polymer (PSF) and nonsolvent (water). Simultaneously, the miscibility between the solvent (NMP) and the nonsolvent (water) causes the diffusional flow of the solvent and the nonsolvent (the solvent and nonsolvent exchange) at several points of the film's top layer and the sublayer, which subsequently leads to the formation of nuclei of a polymer-poor phase. In fact, the low affinity between the PSF chains and water molecules at the points at which water molecules diffuse results in the repulsion of PSF chains and consequently the formation of nuclei of a polymer-poor phase. Because of the continuation of the diffusional flow of the solvent and nonsolvent, the aforementioned nuclei continue to grow until the polymer concentration at their boundaries becomes too high and solidification occurs (the demixing process is completed).

The rate of the demixing process affects the morphology of the membranes. Instantaneous demixing often leads to the formation of bigger pores on the surface and more porous structure in the sublayer, whereas slow demixing results in formation of smaller pores on the surface and denser structure in the sublayer. In the case of slow demixing, nucleation occurs after a certain period of time, and the polymer concentration increases in the top layer. Then, nucleation starts in the inferior layer at short time intervals successively. Hence, the size and composition of the nuclei in the former layer are such that new nuclei are gradually formed in their neighborhood. In other words, in slow demixing, the free growth of limited nuclei (on the top layer) is prevented, and a large number of small nuclei are created and distributed throughout the polymer film. Consequently, contrary to instantaneous demixing, the formation of bigger pores is suppressed, and denser membranes are synthesized.[28,29]

Also, it must be mentioned that finishing the membrane formation (solidification of the cast film in the coagulation bath), causes a halt in reduction of the thickness of the prepared membranes.[30]

Effect of Tetronic-1107. Cross-sectional images of the membranes prepared with the different concentrations of Tetronic-1107 in the casting solution are presented in Figure 3. Also trend of the thickness variation is shown in Figure 4. The SEM images indicate that the addition of small amount of Tetronic-1107 in the casting solution (addition of 2 wt %) can incite formation of the macrovoids. Also the addition of Tetronic-1107 in the casting solution intensifies increasing the thickness (Figure 4) and results in the preparation of membrane with more porous structure in the sublayer (Figure 3).
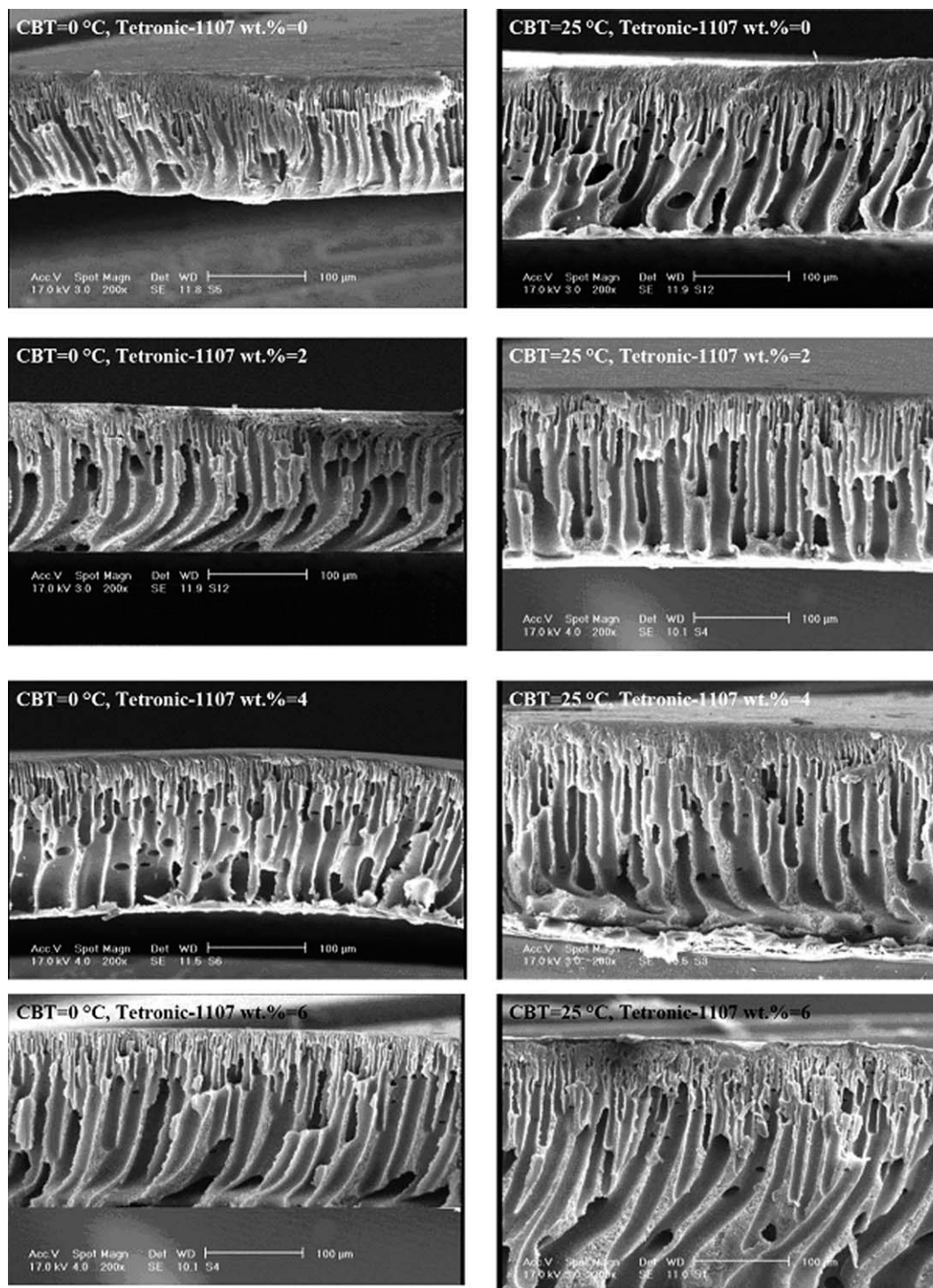
Figure 3. SEM cross-sectional images of the prepared membranes.

The addition of Tetronic-1107 surfactant in the casting solution has two effects on the membrane formation process:

1. Tetronic-1107 is amphiphilic, i.e., with hydrophilic head and hydrophobic tail, and therefore a layer of Tetronic-1107 molecules is formed on the surface of the casting film after immersion into the coagulation bath (Figure 5). Formation of this layer reduces surface tension at the points that surfactant molecules are present and consequently facilitates diffusion of water molecules. This results in the repulsion of PSF chains at mentioned points because of low affinity between PSF and water molecules and consequently formation of nuclei of a polymer-poor phase on the surface. These nuclei subsequently form surface pores. Because of the continuation of the diffusional
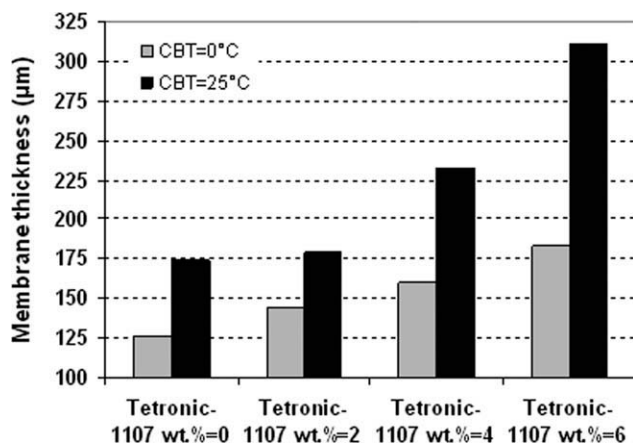
Figure 4. Thickness of the prepared membranes.

flow of the solvent and nonsolvent (water), the nuclei continue to grow until the polymer concentration at their boundaries becomes too high and solidification occurs. Thus addition of Tetronic-1107 results in formation of more nuclei and consequently more pores on the surface.

2. Presence of Tetronic-1107 as a hydrophilic additive with nonsolvent properties increases the thermodynamic instability of the casting solution.

It is evident that above effects result in the instantaneous demixing in the coagulation bath and consequently preparation of the membranes with more porous structure. On the other hands, as mentioned before, instantaneous demixing causes that the solidification of the casting solution in the coagulation bath, and in other words halt of the precipitation process, takes place more quickly. This results in increasing the thickness of the prepared membranes.

Effect of CBT. The effect of variation in CBT with two levels of 0 and 25°C on the membrane morphology is shown in Figure 3. According to this Figure, which presents the cross-sectional images of the prepared membranes, the increase in CBT results in greater formation of macrovoids and approximately more porous structure in the sublayer.

Also the variation effect of coagulation bath temperature on thickness of the prepared membranes is shown in Figure 4. According to this Figure, the decrease in CBT from 25 to 0°C results in noticeable reduction of the thickness of the prepared membranes.

Above important changes in morphology can be attributed to and explained by the phase inversion kinetics. In fact, decrease in CBT reduces mutual diffusivity between the solvent (NMP) and nonsolvent (water) during solidification of the casting solution in the coagulation bath. This results in delayed demixing and consequently causes:

1. Slow growth of nuclei that are poor in terms of PSF and consequently the formation of more nuclei in front of them. The formation of too many nuclei, which grow slowly, results in the formation of smaller pores and consequently denser structure (Figure 3).

2. Stopping of the precipitation process in the coagulation bath takes a long time. It is evident that this delay in

membrane formation results in the precipitation process continuation and consequently decreasing the thickness of the prepared membranes (Figure 4).

The aforementioned observations are in agreement with the literature.[25–27] In general, it can be said that the formation of more porous structure occurs under quick precipitation conditions, and the precipitation is faster at higher temperatures.

Determination of Membrane Surface Morphology, Mean Pore Size, and Surface Porosity Using AFM

Two dimensional surface AFM images of the membranes are presented in Figure 6.

In these figures, the brightest area presents the highest point of the membrane surface and the dark regions indicate valleys or membrane pores. By comparison of the images in Figure 6, it can be observed that the addition of Tetronic-1107 in the casting solution (addition of 2, 4, and 6 wt %) can incite the pores formation in the selected surface area. In fact, the PSF membranes prepared using addition of Tetronic-1107 demonstrate surface consisting of bigger and well-defined depression pores/channels as observed in Figure 6.

On the other hand, by comparison of the images in Figure 6, it can be observed that the size of pores and surface porosity increase by increasing the CBT from 0 to 25°C.

For quantitative analysis, the 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 $\times$ 1 μm area of the membrane surfaces were measured from the height profile of two-dimensional AFM images using SPM software.[24] The height profiles at 10 randomly chosen lines were selected from AFM micrographs. The mean pore size (μ_p) and standard geometric deviation (σ_p) for the membranes were obtained and presented in Table II. The pore size distribution of the membranes was generated on the basis of Eq. (2). The results are presented in Figure 7. As can be observed, there is a change in the pore size distribution for the membranes. The pore size distribution shifted to the right by addition of Tetronic-1107 as a hydrophilic surfactant additive to the casting solution and increasing the CBT (Figure 7).
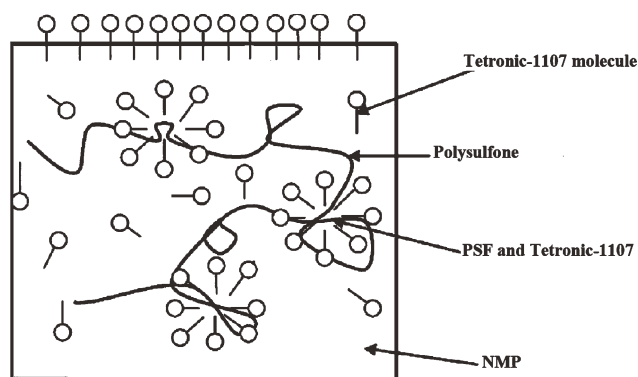

Figure 5. Effect of Tetronic-1107 on the formation of PSF membrane by phase inversion.
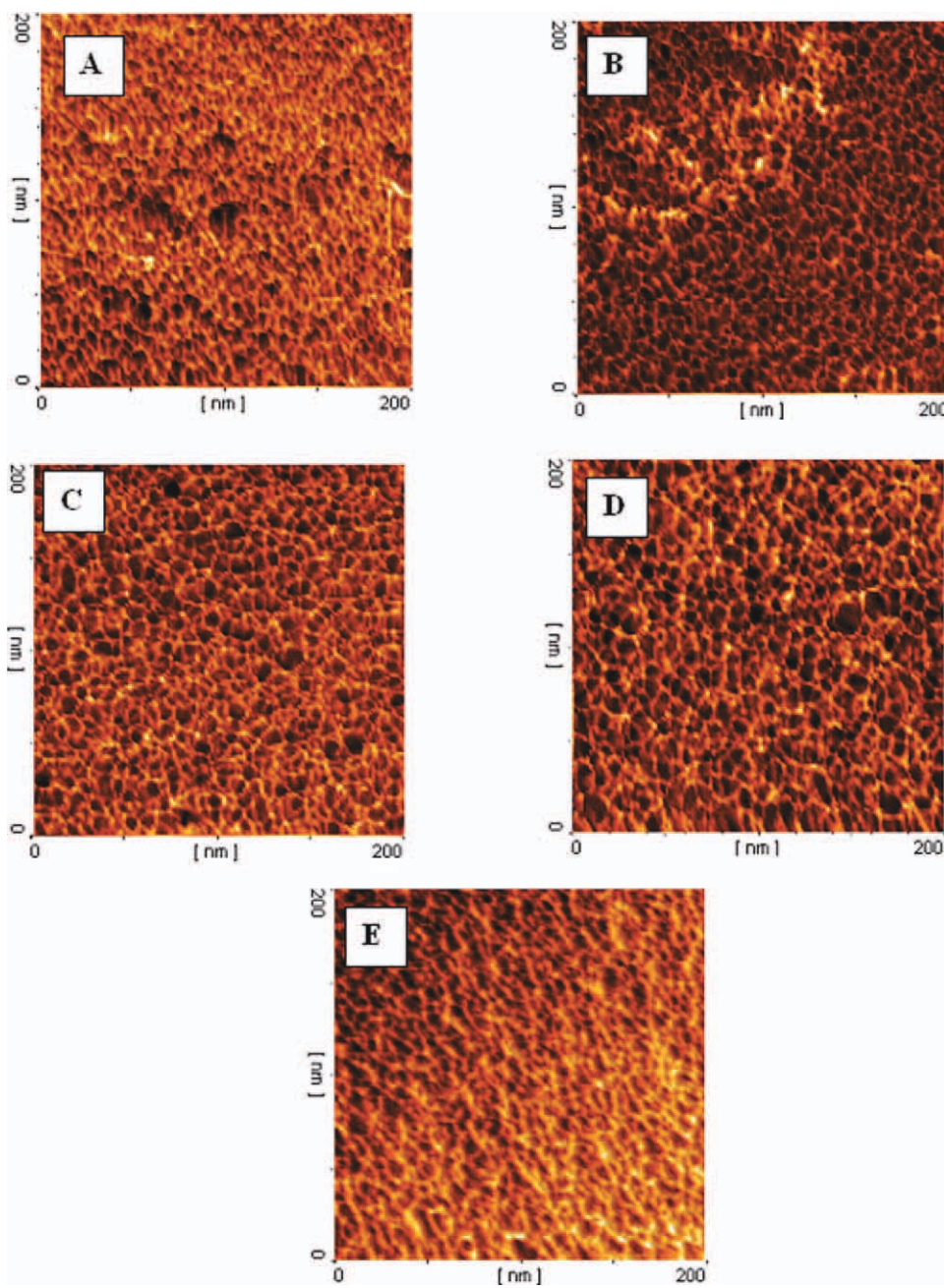
Figure 6. Two dimensional AFM surface images of the prepared membranes: (a) Tetronic-1107 wt % = 0; CBT = 25°C, (b) Tetronic-1107 wt % = 2; CBT = 25°C, (c) Tetronic-1107 wt % = 4; CBT = 25°C, (d) Tetronic-1107 wt % = 6; CBT = 25°C, (e) Tetronic-1107 wt % = 4; CBT = 0°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. The Mean Pore Size and Standard Geometric Deviation Calculated from AFM Images

Tetronic-1107 (wt %)	CBT (°C)	Mean pore size (μ_p nm)	Standard geometric deviation (σ_p)
0	25	7	1.38
2	25	9	1.27
4	25	11.5	1.47
6	25	13	1.52
4	0	8	1.31

The quantitative results of the AFM studies are in agreement with the qualitative results obtained form the SEM images.

Contact Angle

Contact angles were measured to evaluate the changes in the hydrophilicity and surface properties of nanoporous polysulfone membranes after blending with the Tetronic-1107 and variation in CBT. Table III shows the effect of variation in CBT and addition of Tetronic-1107, as a hydrophilic surfactant, on the contact angle and in the other words, wettability of the PSF membranes. As shown in Table III, the highest
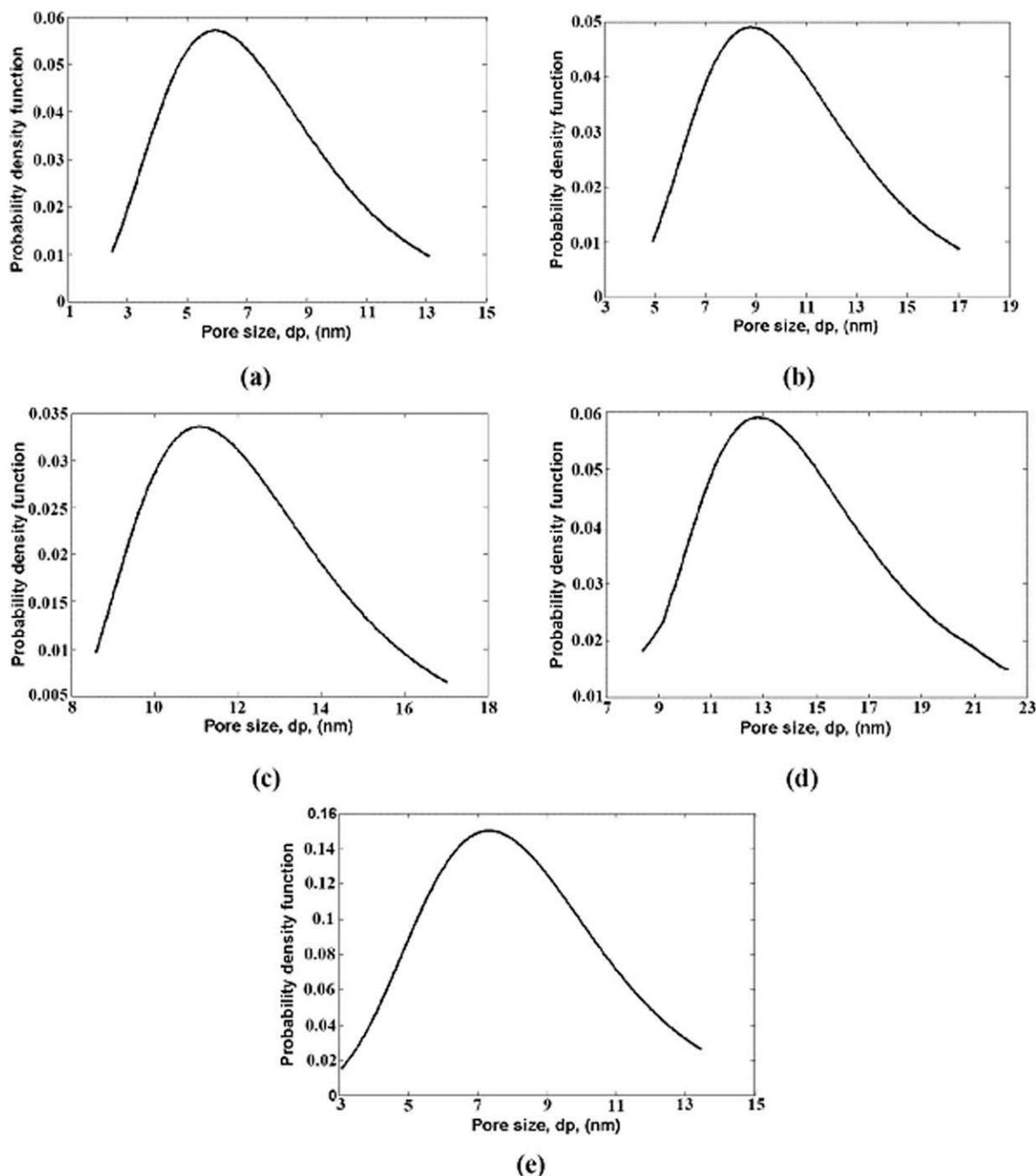
Figure 7. Pore size distribution of the prepared membranes: (a) Tetronic-1107 wt % = 0; CBT = 25°C, (b) Tetronic-1107 wt % = 2; CBT = 25°C, (c) Tetronic-1107 wt % = 4; CBT = 25°C, (d) Tetronic-1107 wt % = 6; CBT = 25°C, (e) Tetronic-1107 wt % = 4; CBT = 0°C.

contact angle for PSF membrane, and in other words the lowest hydrophilicity, is obtained without the addition of Tetronic-1107. When the concentration of Tetronic-1107 in the casting solution is increased, the contact angle of membrane is decreased. This indicates that a more hydrophilic surface is produced by increasing the percentage of Tetronic-1107 in the casting solution.

On the other hand and according to Table III, the increase in CBT from 0 to 25°C results in higher contact angle and conse-

quently lower membrane hydrophilicity. It should be noted that the quantity of the residual Tetronic-1107, that has a direct relationship with the membrane hydrophilicity, determines the wettability of the PSF membranes. The quantity of the residual Tetronic-1107 highly depends on CBT. At higher CBT, because of higher solubility and diffusivity of Tetronic-1107, it can be more easily washed out during the membrane formation process. It is evident that the reduction of residual Tetronic-1107 in the membrane structure results in higher contact angle and

Table III. Contact Angle and Pure Water Permeation Flux (PWF) of the Prepared Membranes

Tetronic-1107 (wt %)	CBT (°C)	Contact angle (°)	PWF (l/m².h)
0	25	73.6	38.5
2	25	64.9	55.3
4	25	58.1	62.9
6	25	55.8	65.7
0	0	70	35.1
2	0	58.6	53.8
4	0	53.2	58
6	0	52.9	62.6

consequently preparation of the membrane with lower hydrophilicity. The aforementioned observations are in agreement with our previous research about the cellulose acetate membranes.[31]

Permeation Properties of the PSF Membranes

Permeation experiments were carried out to study permeability property of the PSF membranes. The obtained results were presented in Table III. As observed, PWF of PSF membranes is increased by increasing the coagulation bath temperature. For example, PWF of membrane prepared into the cold gelation media (CBT = 0°C, Tetronic-1107 wt % = 4) is 57 l/m²h and increases to 62 l/m²h by using a normal gelation media (CBT = 25°C). For porous membranes, pore size and/or pore size distribution in collapsed polymer nodules on the membrane structure are dominating factors in flux variation, compared with free volume in dense polymer structure for nonporous membranes. Even tiny little changes in surface porosity can lead to significant changes in permeate flux. As mentioned before, increase in CBT from 0 to 25°C results in higher surface porosity of the prepared membranes which consequently leads to higher PWF.

On the other hand, PWF of PSF membranes is increased by increasing the Tetronic-1107 concentration. For example, PWF of membrane prepared with no Tetronic-1107 in the casting solution is 50 l/m²h and increases to 64.5 l/m²h by addition 6 wt % of Tetronic-1107 to the casting solution. Increasing PWF of the PSF membranes prepared via addition of Tetronic-1107 as surfactant additive to the casting solution may be due to the combined effects of porosity and hydrophilicity of the PSF membranes. As mentioned before, both porosity and hydrophilicity of the PSF membranes are increased by addition of Tetronic-1107 to the casting solution which consequently leads to higher PWF.

CONCLUSIONS

The effects of Tetronic-1107 concentration as a hydrophilic surfactant additive in PSF/NMP casting solutions and variation in coagulation bath temperature on the fundamental characteristics of the membranes such as morphology (cross-sectional and surface) and wettability were investigated. It was found that:

1. Modified polysulfone membranes with high hydrophilic property can be produced using cold coagulation bath and addition of hydrophilic surfactant, Tetronic-1107, in the casting solution.
2. The membrane thickness is directly related to the CBT and Tetronic-1107 concentration in the casting solution.
3. Membranes with high porosity/bigger pores on the top surface and consequently higher pure water flux can be produced using normal coagulation bath and addition of hydrophilic surfactant, Tetronic-1107, in the casting solution.

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