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Modification of Asymmetric Polysulfone Membrane Surfaces using Mixed Ar/O_2 Plasma Technique†

Chaiporn KAEW-ON[1,2,3,*], Thawat CHITTRAKARN[1,2], Soraya RUANGDIT[1,2], Chalad YUENYAO[4] and Yutthana TIRAWANICHAKUL[1,2]

[1]*Faculty of Science, Department of Physics, Prince of Songkla University, Songkhla 90112, Thailand*
[2]*Membrane Science and Technology Research Center, Prince of Songkla University, Songkhla 90112, Thailand*
[3]*Faculty of Science and Technology, Nakhon Si Thammarat Rajabhat University, Nakhon Si Thammarat 80280, Thailand*
[4]*Department of Physics, Faculty of Science and Technology, Phetchabun Rajabhat University, Phetchabun 67000, Thailand*

(*Corresponding author's e-mail: c.kaewon@hotmail.com)

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Abstract

Asymmetric polysulfone (PSF) membranes for gas separation were prepared via dry-wet phase inversion technique at different conditions such as coagulation bath temperature (CBT) and evaporation time (ET). The thickness of the dense layer that plays an important role on gas selectivity has been investigated by adjusting CBT and ET. Additionally, membranes were treated with mixed Ar/O_2 DC glow discharge plasma in order to modify membrane wettability, surface roughness, and functional groups on the membrane surface. Scanning electron microscopy (SEM) was used to illustrate a cross sectional structure of PSF membranes. Hydrophilic properties of the membrane surfaces were analyzed via water contact angle (WCA) and surface energy measurements. Morphological structures of membrane surfaces, roughness and creation of functional groups were analyzed both before and after plasma treatment by atomic force microscopy and Fourier transform infrared spectroscopy, respectively. Experimental results show that CBT and ET can change porous voids size of the supporting layer and the dense layer thickness underneath of the membrane surface, while a mixed Ar/O_2 gas plasma treatment can enhance hydrophilic properties of the asymmetric PSF membrane surfaces.

Keywords: Coagulation bath temperature, evaporation time, membrane wettability, plasma discharge, surface modification

Introduction

Polysulfone (PFS) is a thermoplastic polymer that is widely used in polymer membrane production because of its appropriate properties, such as high glass transition, high modulus, high thermal and chemical stability [1,2], and it can be easily formed into a film shape [3]. For the preparation of a dense skin layer on to asymmetric membranes a dry or wet phase inversion technique can be used. Membrane properties depend on several factors, for example, solvent evaporation and coagulation bath temperature

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(CBT) [4,5]. Many research groups have used the dry-wet phase inversion technique for membrane forming. Pesek and Koros reported that membranes prepared by a dry-wet phase inversion technique show better selectivity than the ones done via a wet phase inversion technique because they form a dense skin layer on the top of the skin surface; adding a non-solvent will make the dense skin layer to form better [6]. Pakizeh *et al*. [5] studied the effect of CBT on selectivity properties of membranes for CH_4/CO_2 gas separation by applying temperatures of 5, 25, 50, and 80 °C. The result showed that a temperature range of 5 - 25 °C gave a better gas selectivity than higher temperatures. Such the result was resulting from the formation of a dense layer that developed from a higher amount of nuclei, the compactness of polymer chains, and the limited movement of PSF segments around the polymer chains [7]. In addition, Yuenyao *et al*. [8] also studied the effect of solvent evaporation time on the dense skin layer of membranes and they concluded that increase of evaporation time of 0 to 60 s related to increase formation of dense skin layer and sponge-like voids shape in the supporting layer. However, more small porous voids which were developed in the transition layer might affect to efficiency of the separation process [8]. The PSF membrane is a strong hydrophobic polymer due to its high non-polarity property thus it is difficult to change its property by using chemical technical technique and physical technique [9]. Fortunately, the plasma electrical discharges in low energy level (1 - 100 keV) has been widely used to modify material and membrane surfaces because the low energy positive ion and electron particles in plasma discharges can only attack on a few atomic layers underneath the membrane surface but will not affect to the internal membrane structure [10]. Moreover, the membrane surface bombardment with high energy plasma discharge lead to the occurrence of etching processes and chemical bonds breakdowns, such as C-H bonding. Hydrophilic properties of the membrane surface were made by the chemical reconstructed processes with hydrophilic functional groups on the membrane surface [11]. Argon (Ar) gas has been widely used as a working gas since it has a good stability. Many research groups have used Ar plasma due to its inert property and high stability. For this work Oxygen gas (O_2) and Ar mixture was employed as working gases in order to generate a plasma beam for the bombardment of the membrane surface [12-14]. O_2 plasma generates free radical and reconstructed hydrophilic functional groups such as C-O, C=O and OH, etc. [15,16]. This research aims to prepare PSF membranes using dry-wet phase inversion technique and try to enhance the hydrophilic properties of PSF membranes by irradiating membrane surfaces with mixed Ar/O_2 plasma. The CBT and evaporation time (ET) will be adjusted during the process of asymmetric PSF membrane preparation. The increasing of the cross sectional dense layer due to ET and the decreasing of the transitional layer due to CBT will be analyzed by using scanning electron microscopy (SEM).The morphology of the membranes surface roughness will be analyzed for both before and after plasma treatment by atomic force microscopy (AFM). Ageing time of hydrophobic recovering will be analyzed via water contact angle (WCA) and surface energy. Moreover, the Fourier transform infrared spectroscopy (FTIR) will be employed to study the creation of functional groups.

Materials and methods

Materials

Materials for membrane preparation consisted of pellets of PSF, dimethylacetamide (DMAC), ethanol (EtOH), methanol (MeOH), and tetrahydrofuran (THF). Pellets of PSF were supplied by Solvay, China. Non-solvents (ethanol and methanol) and argon-oxygen gas mixtures (Ar/O_2) with ratio of 20:80 %v/v were supplied by Sigma Aldrich and Linde (Thailand) Co. Ltd., respectively. DMAC and THF were purchased from Fluka Riedel-deHaen and Ajax Finechem Pty, respectively. All materials were used as received.

Preparation of asymmetric PSF membranes

Flat sheets of PSF membranes were prepared by dry-wet phase inversion technique. Pellets of PSF were dried for 24 h at 80 °C in a vacuum oven before usage. The dope solution was prepared by mixing 22 wt% PSF, 31.05 wt% DMAC, 31.05 wt% THF, and 15.9 wt% EtOH in a beaker and stirring at room temperature until a homogeneous solution was obtained. The completely dissolved solution was then cast

on a clear glass plate getting the membrane thickness of about 150 microns. A flow chart of the dry-wet inversion method is shown in **Figure 1**. As shown in **Figure 1**, the ET in step 3 was set at 30, 60, 90 and 120 s, while CBT in step 4 was set at 20 and 10 °C.

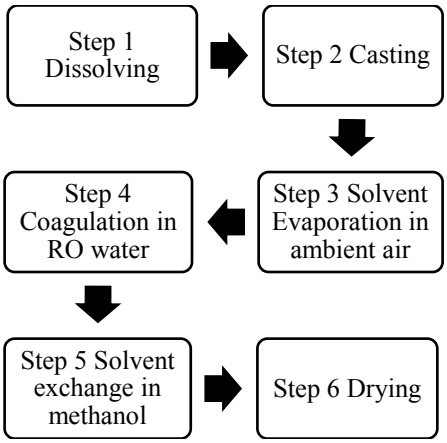


Figure 1 Schematic diagram of membrane preparation by dry-wet phase inversion technique.

Plasma treatment

Asymmetric PSF membranes prepared by dry-wet phase inversion technique were modified by the DC glow discharge plasma. The membrane sample was placed on the anode electrode plate during treatment as shown in **Figure 2**. The discharge gap between cathode and anode electrode was fixed at 3 cm. At the beginning of experiment the plasma chamber was evacuated by 2 stages rotary pump (Edward EDM2). The pressure in the chamber was reduced from atmospheric pressure (1.0 bar) to 0.1 mbar and then the feed gas for generation of plasma discharge would be feed into the chamber by controlling with needle valve. The feeding of the Ar/O_2 gas mixture that are well-mixed in the specific cylinder tank with the ratio of 20:80 %v/v (Thai gas industry, TGI, company) was feed into the plasma chamber until the pressure in the chamber reached to 0.2 mbar [7]. After reach the certain pressure of 0.2 mbar, the DC power supply was turned on to dissociate the mixed gas state to the plasma state at 60 W for 4 min. The schematic diagram of DC glow discharge plasma system for membrane modification is shown in **Figure 2**.

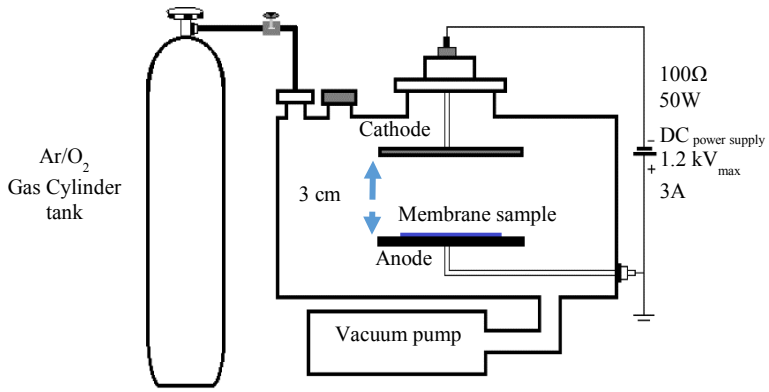


Figure 2 Schematic diagram of DC glow discharge plasma system for membrane treatment.

Characterization

The surface properties of the treated asymmetric PSF membrane were analyzed by various analytical techniques including to SEM, AFM, WCA and FTIR. The top skin layer thickness and pore size structure were analyzed by SEM combined with micrograph and Image J software. Moreover, the surface morphology of the membrane after treatment by DC glow discharges plasma was analyzed by AFM. The WCA was analyzed by WCA machine (Data Physics Instruments GmbH (Germany) model of OCA 15EC). WCA data can be determine the surface energy (SE) for investigating membrane wettability. To study change of chemical interaction on membrane surface, the functional groups on the membrane surface was analyzed by FTIR technique.

Results and discussion

Coagulation bath temperature effect

The membrane cross section measured by SEM is presented in **Figure 3** at magnification around 5000. **Figure 3A** illustrates that the membrane prepared at CBT of 20±2 °C has high amount of small porous voids on the transition layer which lies between the dense skin layer and support layer. This transition layer may reduce the permeation efficiency of the membrane. **Figure 3B** shows a micrograph of a membrane surface prepared at CBT of 10±2 °C. A dense skin layer on top layer is insignificantly changed compared to the membrane prepared with CBT of 20±2 °C of large macrovoids of the supporting layer that provides good pathways for the gas to permeate.

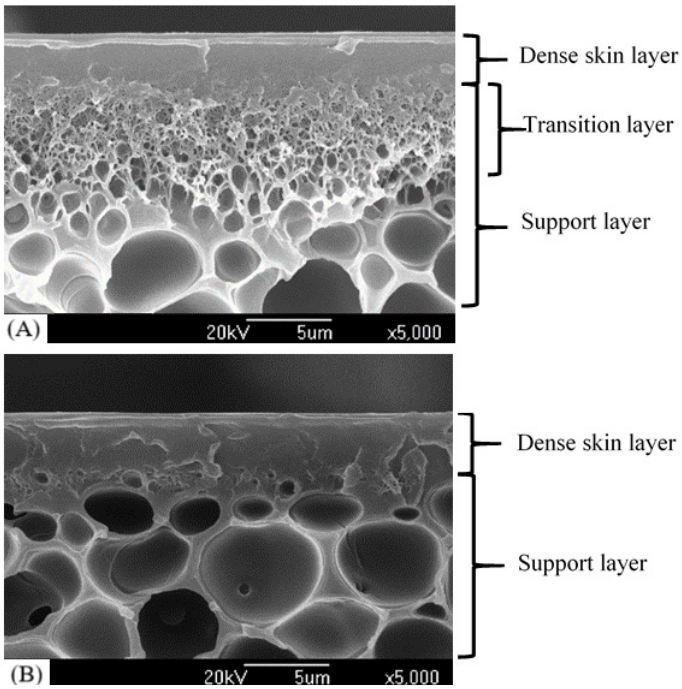


Figure 3 Membrane cross section at different CBT, (A) coagulation with bath temperature of 20±2 °C, and (B) coagulation with bath temperature of 10±2 °C.

Evaporation time

The effect of ET on the morphological structure of the PSF membrane sample after plasma discharge treatment was obviously evaluated through the SEM images together with ImageJ software as illustrated in **Figure 4**. The experimental results stated that the PSF membrane samples with a dense skin layer thickness of 0.42±0.06, 1.42±0.11, 2.35±0.06 and 4.05±0.07 μm were formed when the certain ET was fixed at 30, 60, 90 and 120 s, as shown in **Figures 4A - 4D**, respectively. The formation of a dense membrane layer is mainly caused by solvent evaporation from the PSF membrane surface. During the evaporation of solvent from the membrane surface, the solvent molecules have been moved thus allowing the PSF molecules to replace that space and form a dense skin layer. Therefore, increasing solvent evaporation time will form a thicker dense skin layer [5,6]. This research confirmed the effects of ET on the skin layer thickness of PSF membranes.

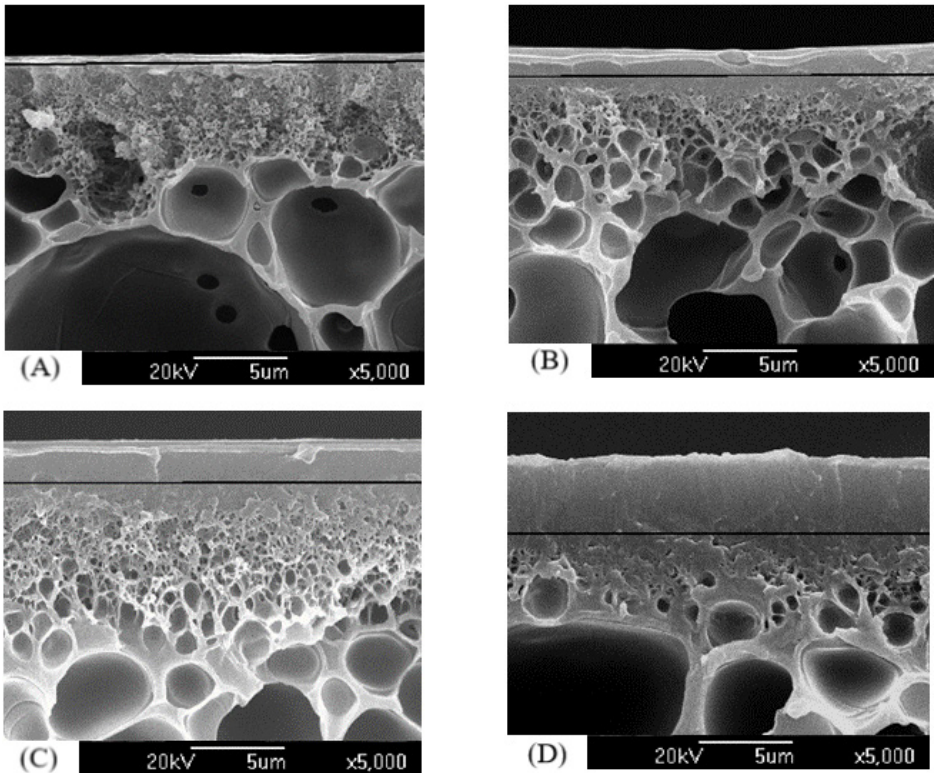
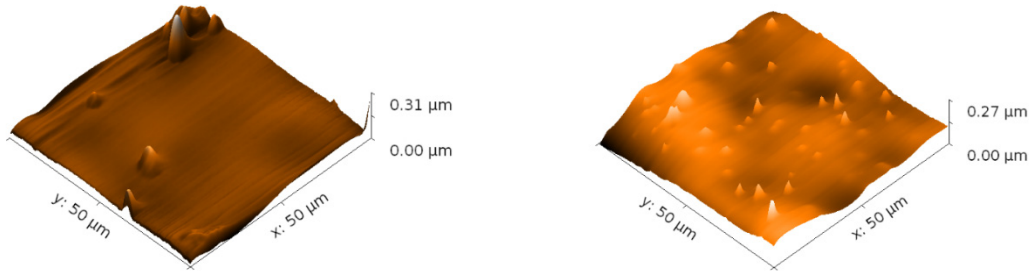


Figure 4 SEM micrograph of cross sectional structure of PSF membrane prepared at ET of (A) 30 s, (B) 60 s, (C) 90 s, and (D) 120 s, respectively.

Plasma treatment

The surface roughness of asymmetric PSF membrane treated by DC glow discharge plasma of Ar/O_2 gas mixtures is shown in **Figure 5**. The root mean square (rms) thickness values before and after plasma treatment are equal to 16.25 and 23.19 nm, respectively. These results indicate that the surface roughness of the membrane is slightly increased.



(A) Before treatment (B) After plasma treatment

Figure 5 Surface roughness of PSF membrane surface (A) before and (B) after plasma treatment observed by AFM.

The WCA of PSF membrane surfaces before and after treatment by Ar/O_2 DC glow discharge plasma are equal to 86.4 and 20.03 degree, respectively. To determine the SE and WCA, formamide and ethylene glycol on the surface of PSF membranes were measured and Eq. (1) [17] was utilized.

$$\gamma_{LV}(1 + cos\theta) = 2(\gamma_L^d \cdot \gamma_S^d)^{1/2} + 2(\gamma_L^p \cdot \gamma_S^p)^{1/2} \quad (1)$$

where γ_S refers to SE of solid consisting of 2 components; polar component (γ_p) and dispersive component (γ_d), while γ_L, γ_{LV} and θ refer to SE of the liquid, the SE between air and liquid and contact angle measured by each liquid, respectively. The SE of membrane treated by Ar/O_2 DC glow discharge plasma and the untreated membrane are shown in **Figure 6**. The results show that plasma treated membranes have approximately a 3 times higher SE than untreated membranes. This result corresponds to the increase of functional groups on the membrane surface measured by FTIR shown in **Figure 7**.

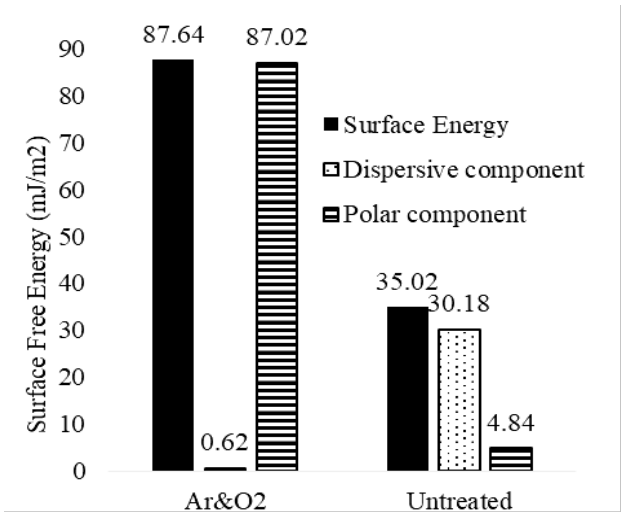


Figure 6 Surface energy of PSF membrane before and after Ar/O_2 DC plasma glow discharge treatment.

In the investigation process of hydrophobic properties of PSF membranes, FTIR was used to study the creation or alteration of functional groups on PSF membrane surfaces both before and after plasma treatment as shown in **Figure 7**. Absorption peaks between wavenumber 3,650 - 3,200 cm^{-1} and 1,650 - 1,750 cm^{-1} indicated the existence of OH and C=O, which are hydrophilic or polar functional groups [2,18]. The results indicate that both hydrophilic functional groups on plasma treated membranes have a higher absorbance percentage than that of untreated membranes. It means that plasma treated membranes have higher hydrophilic properties than untreated ones. This result agrees with the increase of the SE of membrane surfaces treated by Ar/O_2 DC glow discharge plasma.

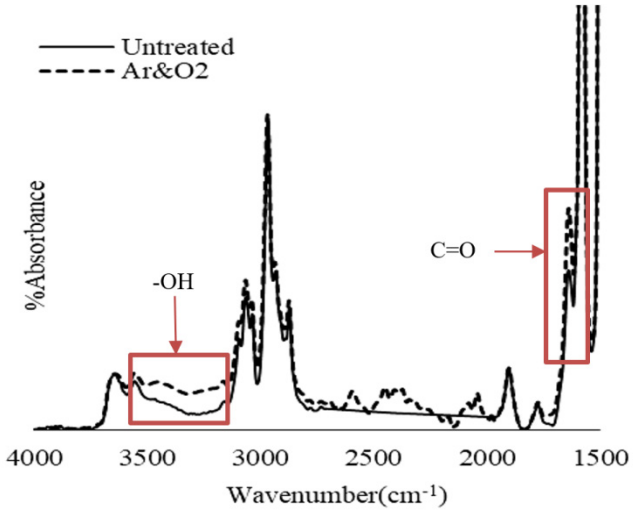


Figure 7 FTIR result of PSF membrane both before and after Ar/O_2 DC glow discharge plasma treatment.

The hydrophobic recovery or ageing effect on PSF membranes surface has been investigated by measuring WCA of both plasma treated and untreated membranes immediately after treatment to 70 days. The results are shown in **Figure 8**. The graph shows a sharp increase of the WCA in the first week; after that the WCA raises only slightly. The uncertainty in the measurement may be due to dispersion of plasmas and the acceptable value should not be more than 5 %.

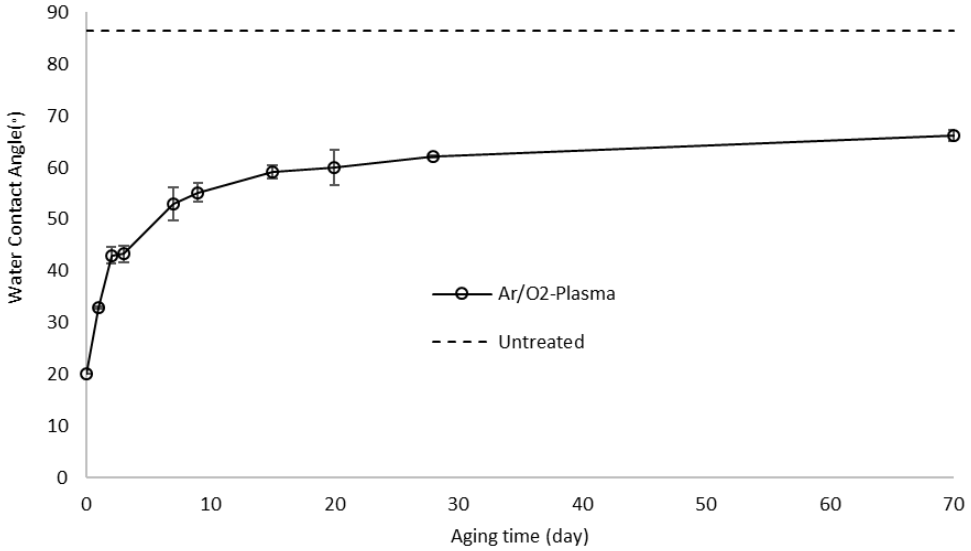


Figure 8 Ageing effect of plasma treated and untreated PSF membrane.

Conclusions

Asymmetric PSF membranes were prepared by dry-wet phase inversion technique where the bulk properties depend on CBT and ET. Higher CBT conditions will induce the creation of a transitional layer between the dense skin and support layer, while at a lower CBT a dense skin layer and the supporting layer was created. In addition, an increase of the ET during membrane preparation will lead to the creation of a dense skin layer with increased thickness. The investigation on the effect of Ar/O_2 plasma treatment on PSF membrane surface has found that WCA decreases to 20.03 degrees or 66 degrees lower than the untreated membranes. The SE of plasma treated membrane is about 87.67 mJ/m^2, which is 2.5 times higher than that of the untreated membranes. Moreover, hydrophilic functional groups such as OH and C=O, and surface roughness were slightly increased after plasma treatment. In addition, the Ar/O_2 plasma treated membranes show a gradual increase of the hydrophobic recovery over 70 days, but still maintains hydrophilic properties.

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