

# Tuning of Preparational Factors Affecting the Morphological Structure and Gas Separation Property of Asymmetric Polysulfone Membranes

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**Abstract.** The aim of this work was to study the effect of preparational factors such as solvent type, evaporation time (ET) and non-solvent additive, on the morphological structure, physical and gas separation properties of the prepared membrane samples by tuning of these parameters. Flat sheet asymmetric polysulfone (PSF) membranes were prepared by the dry/wet phase inversion process combined with the double coagulation bath method. The alteration of the prepared membranes were analyzed through scientific techniques such as Scanning Electron Microscope (SEM) and Dynamic Mechanical Thermal Analysis (DMTA). Furthermore, gas separation performance of membrane samples was measured in term of gas permeation and ideal selectivity of CO<sub>2</sub>/CH<sub>4</sub>. Experimental results showed that the change of preparational factors affected to the gas permeation of asymmetric PSF membranes. For example, the selective layer thickness increased with increasing of ET. This lead to increase significantly of ideal selectivity of CO<sub>2</sub>/CH<sub>4</sub>. The CO<sub>2</sub>/CH<sub>4</sub> ideal selectivity was also increased with increase of ethanol (non-solvent additive) concentration in casting solution. In summary, the tuning of preparational factors affected to morphological structure, physical and gas separation properties of PSF membranes.

## 1. Introduction

Polysulfone (PSF) is one of the most important polymeric materials using for gas separation membrane preparation due to it has many excellent properties such as high mechanical, chemical, and thermal resistance and easy to film-forming. Moreover, the separation and plasticization properties are in the acceptable level [1]. However, the application of PSF gas separation membrane still limited because of its morphological structure, chemical and hydrophilic properties. Several research groups endeavored to improve this limitation by using various techniques. One of the most important techniques used for the preparation of high performance PSF gas separation membranes is the phase inversion process. In this technique, gas separation property can be modified through the manipulation with various parameters including type of solvent and non-solvent and theirs concentrations in the casting solution, the addition of the third component in polymer solution, casting temperature, evaporation time (ET), humidity and pressure. Additionally, the gas separation property of membranes can also be altered by adjustment of the composition and temperature of coagulation media. It was found that the ultra-thin and defect-free dense top skin layer polymeric membranes can be prepared by phase inversion processes incorporated with the dual bath [2,3] and evaporation [4,5] methods. For gas separation membrane preparing from PSF, the permeability is quite low when compared with other polymers [6]. This drawback can improve by changing of membrane configuration through the adjustment of various solvents and other polymers or non-solvent additives as well as the manipulation with composition of coagulation medium. Pakizeh et al. [7] reported that non-solvent additive concentration in the casting solution affected to the gas separation property of PSF membranes.

## 2. Experimental Method

### 2.1. Materials

Pellet of polysulfone (Udel P-1700 NT II) materials were supplied from Solvay, China. Solvents including of Dimethylacetamide (DMAc; 99%, M = 87.12 g/mol), 1-Methyl-2-pyrrolidone (NMP) and Tetrahydrofuran (THF) were purchased from Fluka Riedel-deHaën, Sigma-Aldrich and Ajax Finechem, respectively. Non-solvent including Ethanol (EtOH; C<sub>2</sub>H<sub>5</sub>OH, MW 546.07 g/mol, 99.9%), Methanol (MeOH; CH<sub>3</sub>OH, MW532.04 g/mol, 99.9 %) were supplied by Merck and RCI Labscan. While CO<sub>2</sub> and CH<sub>4</sub> gases with purity of 99.5 % were purchased from Linde Co. (Thailand) Ltd.

## 2.2. Preparation of flat sheet asymmetric membranes

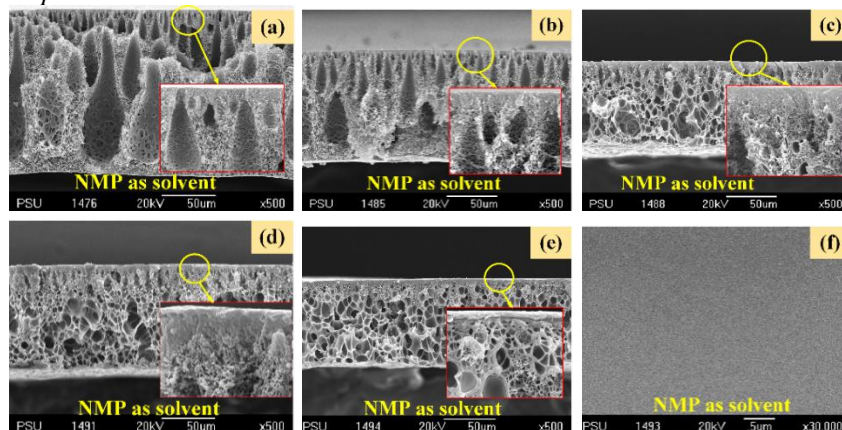
Integrally dense top skin and defect free PSF asymmetric membrane was carefully prepared by the phase inversion process combined with the dual bath method. Firstly, pellet of PSF was dried overnight in electric oven at 85 °C. Dried PSF is gradually poured and dissolved in the solvents at about 55-60 °C. To study the effect of EtOH, the concentration of PSF was fixed at 22.5 wt% while the concentration of EtOH was varied for 14.4-16.9 wt%. The two types of solvent included low and high volatile solvents were used in this study. EtOH and MeOH were used as the non-solvent additive in the casting solution and second coagulation medium, respectively. The completely dissolved solution was sonicated to remove the micro bubble gas. The obtained casting solution was casted on the clear and smooth glass plate. The wet thickness of casted membranes was controlled at 150 μm. To investigate the effect of ET, the nascent membranes are free placed in the normal air for 60, 90, 120, 180 s before it is immersed in coagulation bath of reverse osmosis water for 15 min and methanol for 2.5 h, respectively. After that, the membrane is dried in normal air for 24 h.

## 2.3. Characterizations and gas permeation test

Characteristics of PSF membranes were evaluated through the analytical techniques. Morphological structure was analyzed through the SEM micrograph incorporated with Carnoy Version 2.0<sup>®</sup> Software. Mechanical properties and glass transition temperature (T<sub>g</sub>) were determined by dynamical mechanical thermal analysis (DMTA) technique in tensile mode. Testing frequency and temperature were controlled at 1 Hz and 25-300 °C, respectively. Besides, the permeation of pure CO<sub>2</sub> and CH<sub>4</sub> gases through membrane samples were measured by the gas permeation testing system [8]. Gas pressure was varied in the range of about one to ten bar and at least three PSF membrane samples were tested. The permeation rates are read from soap bubble flow rate meter for 3 times a sample. The average value was presented. The pressure-normalized flux or permeability value in the unit of GPU (1 GPU = 10<sup>-6</sup> cm<sup>3</sup> (STP)/cm<sup>2</sup> s cm Hg) was calculated by using the equation appeared in [8]. In addition, the ideal gas separation factor of CO<sub>2</sub>/CH<sub>4</sub> was estimated by the equation reported in [8].

## 3. Result and Discussion

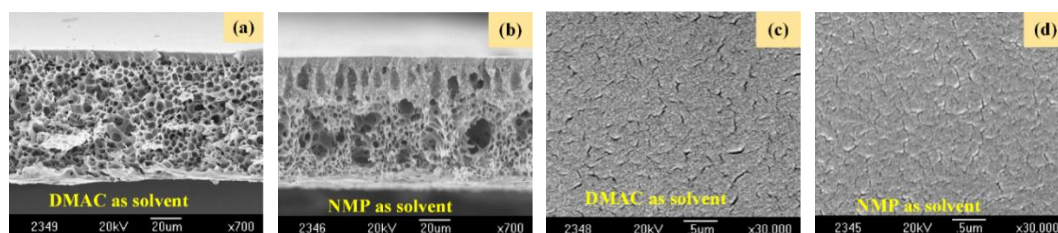
### 3.1. Effect of evaporation time



**Figure 1.** Cross sectional structure at different ET (s); 0 s (a), 30 s (b), 60 s (c), 90 s (d) and 120 s (e), and skin surface (f) of membranes.

Experimental results showed that evaporation time (ET) affects to the dense top skin layer thickness. Skin layer thickness increased with increasing of ET as presented in Fig.1. Additionally, ET was also influenced to the bulk structure that is the water-drop like structure was gradually vanished and replaced with a sponge-like structure when ET increased up to 120 s. Pore is not appeared on the top skin surface as illustrated in Fig.1(f). This confirmed the really dense top skin layer. Morphological structure of prepared PSF membrane directly affects to the pressure-normalized flux or permeance and selectivity of gas through the membranes.

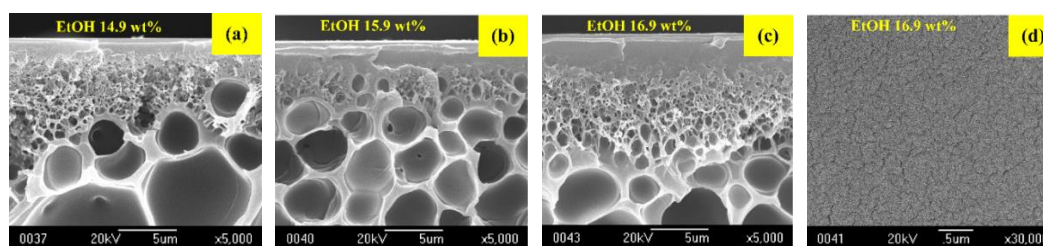
### 3.2. Effect of two solvent types



**Figure 2.** Cross sectional structure ((a), (b)) and top skin surface ((c), (d)) of membranes prepared from casting solution using DMAC and NMP as solvents.

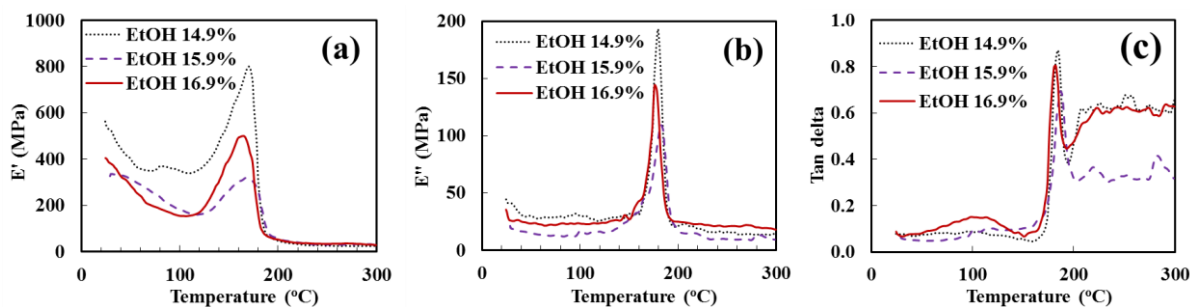
Fig. 2 shows the morphological structure of PSF membranes prepared by using DMAC and NMP as solvents. It was clearly that solvent type affected to the morphological structure of PSF membranes. Sponge-like structure appeared when DMAC was used as solvent as presented in Fig.2(a). Finger-like porous structure and macrovoid created when DMAC was replaced with NMP as shown in Fig.2(b). The difference of cross sectional structure may affected from the properties of solvents. It was shown in Fig.2(c) and (d) that the pore not appeared on the top skin surface of both the membranes preparing from NMP and DMAC.

### 3.3. Effect of non-solvent additive



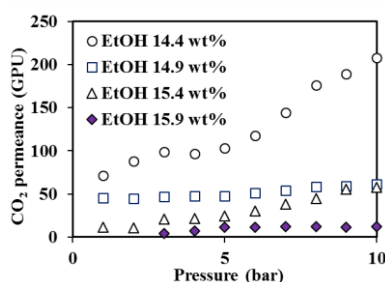
**Figure 3.** Alteration of selective layer thickness ((a), (b), (c)) and top skin surface (d) of PSF membranes at different EtOH concentration.

In addition to the effect of ET and solvent type, the effect of non-solvent additive was determined. Concentration of EtOH clearly affected to the skin layer thickness of PSF membranes is that skin layer thickness gradually increase with increasing of EtOH concentration as shown in Fig.3(a) to (c). Additionally, as shown in Fig.3(d), the pore not appeared on the top skin surface. Fig.4(a) to (c) showed the effect of EtOH concentration on the physical properties of PSF membranes. Modulus of PSF membrane trends to decrease when the concentration of EtOH was increased. However, EtOH concentration do not affected on glass transition temperature ( $T_g$ ). Gas permeation testing result, as shown in Fig.5, showed that  $\text{CO}_2$  permeance decreased with increasing of EtOH concentration in the casting solution. Besides, EtOH concentration also affected on the  $\text{CH}_4$  permeance. Variation of gas permeance related to the alteration of morphological structure of PSF membranes that was mentioned above. From this study, we found that the ideal  $\text{CO}_2/\text{CH}_4$  selectivity is about 34 at EtOH concentration of 16.4 wt%.



**Figure 4.** Physical properties change of PSF membranes prepared at different EtOH concentration

### 3.4. Gas separation performance



**Figure 5.** CO<sub>2</sub> permeation through PSF membranes at different EtOH concentrations

## 4. Conclusion

It was confirmed from the experimental results that alteration of preparation factors affected to the morphological structure as well as physical and gas separation properties of PSF membranes.

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