Synthesis and characterization of nanoporous polyethersulfone membrane as support for composite membrane in CO₂ separation: From lab to pilot scale

Dongzhu Wu, Lin Zhao, Varun K. Vakharia, Witopo Salim, W.S. Winston Ho*

William G. Lowrie Department of Chemical and Biomolecular Engineering,

Department of Materials Science and Engineering,

The Ohio State University, 151 West Woodruff Avenue, Columbus, OH 43210-1350, USA

* Corresponding author. Tel.: +1 614 292 9970; fax: +1 614 292 3769.

E-mail address: ho.192@osu.edu (W.S.W. Ho).

Abstract

Nanoporous polyethersulfone (PES) membranes were prepared from PES/*N*-methyl-2-pyrrolidone (NMP)/2-methoxyethanol (2-ME) casting solutions with water as coagulant by both vapor- and non-solvent-induced phase inversion steps successively under various preparation parameters. 2-ME was incorporated into the casting solution as a pore-forming additive because of its high affinity with water, leading to more open membrane morphology. A detailed study of the effects of different parameters, including polymer concentration, 2-ME/NMP ratio, relative humidity, water vapor exposure time, and water coagulation bath temperature, was conducted in lab-scale experiments to determine the operation guidelines for pilot-scale fabrication. 14-inch wide PES membranes were fabricated successfully by using a continuous casting machine. Parametric studies in pilot-scale fabrication were also carried out. Surface morphologies of PES membranes were characterized by scanning electron microscopy (SEM). The morphological differences between both scales by the same preparation conditions were compared. Based on the guidelines established from lab-scale experiments, the casting solution composition and coagulation bath temperature were optimized in a pilot-scale continuous casting machine to fabricate the 14-inch wide PES membrane with a desired morphology suitable for use as the substrate of composite membranes in CO₂ separation. The studied fabrication process also showed the potential for the commercial production of the PES membrane in a larger scale by the vapor- and non-solvent-induced phase inversion technique.

Keywords: PES membrane; Phase inversion; Surface morphology; CO₂ separation; Lab to pilot scale

1. Introduction

Synthetic microfiltration (MF) and ultrafiltration (UF) membranes, such as those applied in food engineering, medical science, and water treatment, as well as nonporous membranes used in gas separation and pervaporation, are mainly prepared by a phase inversion technique [1,2]. Researchers have been making tremendous progresses since the development of the acetate cellulose reverse osmosis membrane by Loeb and Sourirajan in 1960s [3]. Phase inversion is a technique that can transform the liquid-state membrane to the solid-state membrane in a controlled manner throughout the membrane from its surface to its bulk. The final morphology of the membrane is the key factor that determines the performance of the membrane application. Therefore, many studies have been conducted to obtain the desirable membrane morphologies for various applications.

Phase inversion processes fall into four categories: 1) evaporation of the solvent and non-solvent, 2) exposure to the non-solvent vapor, i.e., vapor-induced phase inversion (VIPI), 3) immersion into the non-solvent coagulation bath, i.e., non-solvent induced phase inversion (NIPI), and 4) thermally induced phase inversion (TIPI) by lowering the casting solution temperature [4–6]. Combining the abovementioned VIPI and NIPI processes together, also known as the dry-wet phase inversion technique, is a popular method for asymmetric polymer membrane preparation. Many factors, such as polymer concentration, non-solvent additive, vapor exposure time, and coagulation bath temperature, could affect the chemical and physical properties of the membrane significantly [7,8].

It is well documented that the addition of non-solvent in the casting solution improves the porosity of the membranes as well as the surface properties, such as hydrophilicity [9,10]. Wang et al. studied the effect of alcohol additives on the morphology of the PES membrane [11]. Their

work pointed out that the non-solvent additive could be one of the most important parameters to control the membrane morphology, and provided the guidelines of choosing a suitable solvent/non-solvent additive pair. Li et al. showed that the introduction of diethylene glycol, a low molecular weight (MW) non-solvent additive, could slow down the precipitation rate and change the cross-section morphology from a macrovoid to a spongy-like structure [12]. Shin et al. investigated the effect of 2-ME on the membrane morphology in both vapor-induced and non-solvent induced steps of the phase inversion process [4]. Their observations suggested that the introduction of 2-ME could not only suppress the macrovoid formation but also enlarge the surface pore size.

Furthermore, a vapor exposure step prior to the non-solvent immersion precipitation is crucial since the effect of the vapor on the skin layer can also affect the solvent and non-solvent exchange rate significantly in the subsequent process. A study by Caquineau et al. demonstrated that the non-solvent vapor introduced nuclei on the skin layer that could grow into a cell-like structure [13]. Tsai et al. obtained the evidence that the membrane morphology could be controlled by vapor-induced phase inversion. They showed the disappearance and appearance of the macrovoids by varying the air-gap length and relative humidity [14]. Shin et al. also reported that a longer exposure time to the water vapor or a higher relative humidity resulted in a bigger pore size because of the growth of nuclei on the membrane surface [4]. Studies by Kang et al. indicated that the formation of surface pores during the vapor-induced step was an important parameter for controlling the final pore size of the membranes as it could affect the solvent/non-solvent exchange [15,16].

In addition, as the fast solvent and non-solvent exchange occurs in the coagulation bath, conditions and types of coagulants are key parameters in determining the morphology of the

membrane. Buonomenna et al. discussed the effect of coagulation conditions and coagulant types [17]. Boom et al. developed a diffusion model for the phase inversion in a quaternary system and explained the coagulation bath effect on the membrane morphology from the modeling point of view [18]. All of those works have indicated the importance of the preparation parameters in determining the final membrane morphology in the dry-wet phase inversion process.

Though dry-wet phase inversion was explored and reported extensively in the literature [4–18], PES membranes prepared by this technique were mainly applied in MF and UF. However, a novel application of the PES membrane is as the support material, to provide mechanical strength, for composite membranes in gas separation. One of the most important membrane applications for gas separation is CO₂ separation and capture [19–22]. The increasing emission of CO₂ is a major air pollution problem, resulting in the global climate change [19,20]. CO₂ capture and sequestration are crucial to resolve this current environmental issue [20,22]. Membrane, with its ease of operation, energy efficiency, and system simplicity, has become one of the most widely studied technologies for CO₂ removal from flue gas and syngas over the past decades [22]. Ho et al. developed the facilitated transport membranes containing amino groups to effectively separate CO₂ from a gas mixture [21–24]. Wang et al. established the polyvinylamine (PVAm)-piperazine (PIP) and PVAm-ethylenediamine (EDA) composite membranes for CO₂ removal from flue gas [25,26]. Hägg et al. also studied the PVAm-based composite membrane for post-combustion CO₂ separation [27]. These three research groups have applied polysulfone (PSF) nanoporous membranes as the substrates for their selective layers. PS, PES, cellulose acetate (CA), and polyacrylonitrile (PAN) membranes are commonly employed as the substrate materials [8]. However, as for PVAm-based composite membranes,

the hydrophobic nature of PSF membrane results in an adhesion issue between the polymeric selective layer and the support material. Therefore, PES, with its less hydrophobic property compared to PSF, as well as its excellent thermal and mechanical resistances, has gained the most attention as the substrate in composite membranes [7,8]. Moreover, the morphology of the substrate is critical in achieving a high CO₂ permeance since an open substrate has less resistance for gas permeation. Both studies by Li et al. [28] and Shieh and Chung [29] reported that an open morphology of the substrate could reduce the mass transfer resistance in general, but it could also induce the penetration of the top selective layer during coating. This suggests that an optimal substrate pore size and porosity are required to optimize the CO₂ permeance of a composite membrane. A suitable surface morphology is important in achieving the optimum performance of a composite membrane [30].

In order to meet the various requirements of the substrate materials for composite membranes in gas separation, a desired morphology is needed for PES membranes. As a result, it is necessary to study the phase inversion system in lab scale to determine the effect of each parameter. Furthermore, the most up-to-date membrane systems for carbon capture from flue gas require a membrane area in the range of 1.5 – 3 million m² [23,31]. One essential prerequisite to satisfy such a huge demand is the mass production of the membrane substrate, such as the nanoporous PES membranes, in a controllable manner. Although pilot-scale fabrication of hollow-fiber PES membranes by the dry-wet phase inversion technique was reported in literature [14,28,30], very few studies described the pilot-scale fabrication of flat-sheet membranes via the phase inversion technique. Only one reference mentioned the apparatus for the continuous fabrication of flat-sheet membrane in pilot scale was identified [32]. But, its main focus was on the compositional point of view instead of fabrication parameters. Therefore,

with the lack of available information in the literature, we studied the fabrication of PES membranes in pilot scale based on the conditions defined in lab scale in this work.

This paper describes the comparison of the lab-scale and pilot-scale PES membrane fabrication, as well as the development of the pilot-scale PES fabrication process with a desired morphology by using vapor- and non-solvent-induced phase inversion steps successively. Firstly, a lab-scale casting procedure consisting of the steps shown in Fig. 1-a was studied. Each parameter that could affect the membrane morphology was investigated in detail to provide guidelines for pilot-scale fabrication. The investigated parameters included casting solution composition, water vapor exposure time, relative humidity, water coagulation temperature, and PES layer thickness. Secondly, a pilot-scale continuous process using the casting machine equipped with a humidity chamber shown in Fig. 1-b was developed. Fig. 1-c shows the final product of the pilot-scale 14-inch wide PES membrane. Operational parameters that contribute to the final desirable morphology were discussed. Moreover, a simplified diffusion model elucidating the non-solvent flux in the coagulation bath to affect membrane morphology was developed. Generally speaking, this study explored the potential commercial capability of the mass production of PES membranes with required surface morphology as substrates for gas separation.

Fig. 1. PES preparation and apparatus: a. Lab-scale preparation procedure; b. Pilot-scale continuous casting unit; and c. 14-inch wide PES membrane product.

2. Experimental

2.1. Materials

PES (Ultrason[®] E7020P, MW 92000 g/mol) flakes donated by BASF (Wyandotte, MI, U.S.A) were dried at 120°C in the vacuum oven for 12 hours before use. Polyester nonwoven fabric was provided by TriSep Corporation (Goleta, CA, U.S.A). NMP and 2-ME were purchased from Sigma-Aldrich Chemical Co. and Fisher Scientific Co., respectively. Glycine (98.5%), piperazine (99%), and sodium dodecyl sulfate (SDS) were also purchased from Sigma-Aldrich Chemical Co. High MW PVAm was synthesized in our lab, and the synthesis method was described in a published reference [33]. All chemicals were used without any further purification.

2.2. PES membrane preparation

The PES membranes were prepared via vapor- and non-solvent-induced phase separations in both lab and pilot scales. First, the casting solutions were prepared by dissolving PES into an appropriate amount of NMP under magnetic stirring at 80°C for 3 hours for lab scale and overnight for pilot scale, until the solution was clear and homogeneous. Then, the solution was cooled down to room temperature, and 2-ME was added dropwise to minimize phase separation. The solution was kept continuously under magnetic stirring overnight. All the procedures were carried out under a nitrogen shower.

In the lab-scale membrane preparation shown in Fig. 1-a, the solution was cast on a flattened nonwoven fabric taped on a glass plate by using the GARDCO stainless-steel film applicator (Paul N. Gardner Company, Pompano Beach, FL, U.S.A.). The wet film was exposed to water vapor humidified nitrogen with controlled relative humidity for a period of time and then immersed into a water bath at a particular temperature. Eventually, a solid PES layer was formed on the nonwoven fabric. The sizes of all prepared lab-scale PES membranes were 3 inches by 4 inches. The membrane thickness was kept $\sim 28 - 30 \mu\text{m}$, above the fabric, by maintaining the same gap setting ($107 \mu\text{m}$) of the film applicator in order to avoid the thickness effect that will be discussed in a later section.

In pilot-scale membrane fabrication, as shown schematically in Fig. 2, the solution was cast continuously onto the nonwoven fabric (14-inch wide) moving at a particular web speed by a stationary stainless-steel casting knife with the pre-determined gap setting ($94 \mu\text{m}$). A proper tension was applied to ensure the flatness of the fabric and the uniformity of the cast film. The trough holding the casting solution was purged with nitrogen at a sufficient flow rate to prevent the casting solution from phase separation caused by ambient humidity. A humidity chamber was installed after the casting knife, and the rolling speed of the fabric controlled the exposure

time in the humidity chamber. Subsequently, the cast film was immersed into a water tank at a given temperature to form the PES membrane. The fabricated PES membrane was kept in water for additional 24 hours to ensure the removal of residual NMP and 2-ME.

Fig. 2. Schematic diagram of the pilot-scale continuous casting machine.

2.3 Selective layer preparation

In the preparation of the selective layer, high MW polyvinylamine (PVAm) serving as a fixed carrier and piperazine glycinate (PG) being a mobile carrier were used [33]. SDS was incorporated for a better adhesion between the selective layer and the PES substrate. The detailed membrane preparation procedures were described in a published reference from our group [33]. A PVAm/PG weight ratio of 65/35 was selected, and 5 wt% SDS in the total solid was chosen based on the data reported elsewhere [33]. The membrane was cast using a film applicator with an appropriate gap setting, for a thickness of ~ 150 nm, on the PES substrates. The membrane was characterized for CO₂ separation using a gas permeation apparatus, of which the schematic diagram has been reported elsewhere [21,22,24].

2.4. Characterization of PES membrane properties

The zero-shear viscosity of the casting solution was measured by Brookfield DV-E viscometer (Middleboro, MA, U.S.A.). The surface morphologies of the PES membranes and the thicknesses of the selective layers were determined by scanning electron microscopy (SEM, FEI Nova 400 NanoSEM, Hillsboro, OR, U.S.A.). All the images were analyzed by Clemex Vision Professional Edition (Longueuil, Quebec, Canada) software to obtain average pore size and surface porosity.

The gas transport properties of the PES substrate and composite membranes were tested by using the gas permeation unit reported previously [24]. The membrane was installed into the stainless-steel testing cell with an effective area of 3.4 cm² and tested with a typical simulated flue gas condition. A binary gas mixture containing 20% CO₂ and 80% N₂ (on a dry basis), with a flow rate of 60 ml/min controlled by mass flow meter (Brooks Instrument, Hatfield, PA, U.S.A.), was applied as the feed gas. Argon, with a flow rate of 30 ml/min, was used as the sweep gas. The feed and sweep side pressures were adjusted to be 1.5 psig and 1.2 psig, respectively. Both of the gases were saturated with water vapor at 57°C, and the membrane was tested at this temperature inside an oven with a temperature controller (Bemco Inc., Simi Valley, CA, U.S.A.). The gas sample compositions in the feed, retentate and permeate streams were analyzed by a gas chromatograph (Model 6890N, Agilent Technologies, CA, U.S.A.). The testing conditions were selected to simulate the composite membrane testing for CO₂ capture from flue gas.

3. Results

3.1. Lab-scale PES membrane preparation

3.1.1. Effect of polymer concentration

In general, a higher polymer concentration in the casting solution results in a higher solution viscosity. The viscosities of the casting solution with different polymer concentrations at room temperature are shown in Table 1. Fig. 3 shows that both average pore size and surface porosity reduce significantly by increasing the polymer concentration with the other preparation parameters, such as 2-ME/NMP weight ratio, vapor exposure time, relative humidity and water coagulation bath temperature, maintained the same. Strathmann et al. reported that increasing the polymer concentration, and consequently increasing the viscosity of the solution, promoted the precipitation of the polymer and hindered the diffusion of the non-solvent to the cast film [34]. As a result, the porosity of the membrane reduced as the polymer concentration increased [35,36]. The polymer membrane solidified more rapidly in a higher polymer concentration solution than a lower one. Consequently, the pores could not grow into larger ones if the concentration was high, which coincided with the results shown in Fig. 3. As a high porosity was required for a lower resistance in gas transport and a suitable viscosity was necessary for casting on a fabric, the polymer concentration of 12 wt% was chosen for the subsequent lab-scale studies.

Table 1. The effect of polymer concentration on casting solution viscosity.*

Polymer concentration (wt%)	Viscosity (cp)
11	331
12	403
13	497
14	603
15	710
16	830
17.5	978

* All solutions were prepared with the upper limits on their 2-ME/NMP weight ratios as shown in Table 2.

Fig. 3. Effect of polymer concentration on the average pore size and porosity of the PES membrane surface.

3.1.2. Effect of 2-ME/NMP weight ratio

2-ME, as a non-solvent, has a solubility limit with respect to a certain polymer concentration. Table 2 lists the various upper limits of the 2-ME/NMP weight ratio for different polymer concentrations. A lower weight ratio of 2-ME/NMP is needed in order to achieve a homogeneous solution without any phase separation at a higher polymer concentration. Fig. 4 shows the surface morphologies of the PES membranes with different 2-ME/NMP weight ratios. As shown in this figure, by increasing the ratio from 15/35 to 60/35, the pore size and porosity increase from 26.7 nm and 9.7% to 48.6 nm and 14.4%, respectively. Two main functions of the addition of non-solvent in casting solution reported in the literature are: 1) suppress the formation of macrovoids in the cross-section of PES membrane and 2) increase the porosity of the membrane because it introduces more nuclei in the bulk of the casting solution that are

further transformed into an interconnected structure [37,38]. Shin et al. showed that the addition of 2-ME could facilitate the formation of spongy structure and increase the porosity of the PES membrane [4]. Because of the high affinity of 2-ME with water, the surface layer of the cast film would absorb more water vapor. As a result, more water nuclei were introduced, which further grew into bigger pores on the surface during the precipitation step.

Table 2. The upper limits of 2-ME/NMP weight ratios for different polymer concentrations.

Polymer concentration (wt%)	Upper limit of 2-ME/NMP weight ratio
11 – 13	60/35
14 – 15	58/35
16	54/35
17 – 18	52/35

Fig. 4. Effect of 2-ME/NMP weight ratio on the average pore size and porosity of the PES membrane surface.

3.1.3. Effects of relative humidity and exposure time

Figs. 5 and 6 illustrate the surface morphologies of the PES membranes with various relative humidities and water vapor exposure times, respectively. The results showed that both pore size and porosity increased at higher relative humidity and longer water vapor exposure time. In

vapor-induced phase inversion, non-solvent vapor introduces nuclei on the surface layer [4]. Two major factors are involved with high relative humidity and long water vapor exposure time. On one hand, the solvent in the wet film evaporates to some extent by exposing to water vapor. Therefore, the polymer concentration in the skin layer increases, leading to a dense polymer phase. On the other hand, the skin layer also absorbs water from the humid surrounding at the same time. The water absorption generates nuclei in the polymer phase, which leads to the formation of pores. The pores grow with the diffusion of solvent from the surrounding polymer phase. In the meantime, the polymer concentration in the polymer phase increases. However, the pores stop growing when the polymer concentration in the polymer phase enters the solidified region in the phase diagram [4,39]. Since these two factors during the vapor-induced phase inversion stage have opposite effects on the surface morphology, there is an optimum balance for the abovementioned two processes in order to achieve a desired surface morphology [13]. The results from this study were consistent with the literature results.

Fig. 5. Effect of relative humidity on the average pore size and porosity of the PES membrane surface.

Fig. 6. Effect of water vapor exposure time on the average pore size and porosity of the PES membrane surface.

3.1.4. Effect of water coagulation bath temperature

Fig. 7 shows the surface morphologies of the PES membranes formed at different water coagulation bath temperatures. As observed, the pore size and surface porosity increased by elevating the temperature from 23 °C to 60 °C. These observations were in line with the literature [36]. However, the increase was more significant in the range of 23 °C to 45 °C than 45 °C to 60 °C. Therefore, most of the membranes were prepared at 45 °C in this lab-scale study. Coagulant temperature affects the kinetics of phase inversion significantly [40]. Generally, a higher coagulation bath temperature results in a more porous membrane since the solvent and non-solvent exchange rate is higher. In other words, an elevated water temperature provides increased solvent and non-solvent diffusion rates before solidification of the cast film in the quenching stage [41]. In this case, a faster precipitation accompanied with a larger pore size and a higher porosity occurs [42].

Fig. 7. Effect of the water coagulation bath temperature on the average pore size and porosity of the PES membrane surface.

3.1.5. Effect of polymer layer thickness

Li et al. have reported the thickness dependence of the membrane structure in wet phase inversion [43]. Though they did not report on surface morphology, they pointed out clearly the effect that the increased membrane thickness changed a spongy structure to a fingering-like structure. In our study, as shown in Fig. 8, the pore size and porosity reduced as the thickness of the membranes increased. The effect was very significant when the membrane thickness exceeded 30 μm . A thicker wet film provided a higher resistance for non-solvent diffusion during the immersion step. As a result, the surface morphology was less open in a thicker PES membrane.

Fig. 8. Effect of PES layer thickness on the average pore size and porosity of the PES membrane surface.

3.2. Pilot-scale PES membrane fabrication

As mentioned previously, although the lab-scale synthesis of PES membranes has been studied extensively [4–17], the PES membrane fabrication in pilot scale, to our best knowledge, has not been reported much. With the requirements for composite membrane preparation in a pilot quantity, it is necessary to study the factors that affect the final PES membrane morphology in pilot scale. From the operational points of view for the pilot-scale casting machine, a certain web speed and tension were required for a smooth fabrication of PES membrane based on initial trial runs. Therefore, the water vapor exposure time was fixed (~ 6.25 sec) since it depended only on the time for the web to pass through the humidity chamber. Moreover, previous lab-scale results showed that the effect of the relative humidity higher than 60% was not as pronounced; therefore, relative humidity of 60% was chosen for the simplicity of operation. As a result, there were only two adjustable parameters in the pilot-scale unit operation, which were the casting solution composition and the water coagulation bath temperature.

3.2.1. Effect of casting solution composition

The results of lab-scale PES membranes showed that the polymer concentration in the casting solution affected the morphology significantly. In general, a higher polymer concentration resulted in smaller pore size and lower porosity. However, with the addition of the non-solvent, the upper limit of the 2-ME/NMP weight ratio varied with different PES concentrations as pointed out in the lab-scale experiments. As a higher amount of 2-ME increased the pore size and porosity, the highest 2-ME/NMP weight ratios were chosen for different concentrations in order to obtain open morphologies. Therefore, the PES concentrations with the upper limit 2-ME/NMP ratios ranging from 12.5 wt% to 18 wt% were studied in details in pilot scale. As listed in Table 3, by increasing the PES concentration from 12.5 wt% to 18 wt%, both the pore size and porosity reduced from 69.4 nm and 17.1% to 46.8 nm and 10.7%, respectively. Fig. 9 shows the corresponding SEM images of surface morphologies with various concentrations. It should be noted that the effect of the PES concentration on the morphology was less significant in pilot scale than in lab scale as shown in Fig. 3. This was mainly due to the higher solvent/non-solvent exchange rate in pilot scale, which will be discussed in Section 4.

Table 3. Effect of polymer concentration on the pilot-scale PES membrane morphology ^{a, b}.

Membrane No.	PES con. (wt%)	2-ME/NMP	Pore size (nm)	Surface porosity (%)
M-1	12.5	60/35	69.4	17.1
M-2	13	60/35	68.9	17.0
M-3	14	58/35	67.1	16.5
M-4	16	54/35	56.1	14.1
M-5	17	54/35	51.5	11.8
M-6	18	52/35	46.8	10.7

❖ ^a All the polymer casting solutions were kept at 26°C.

❖ ^b The water coagulation bath was kept at 26°C.

Fig. 9. SEM images demonstrating the effect of polymer concentration on the surface morphologies of the pilot-scale PES membranes: a. M-1 (12.5 wt%); b. M-2 (13 wt%); c. M-3 (14 wt%); d. M-4 (16 wt%); e. M-5 (17 wt%); f. M-6 (18 wt%).

3.2.2. *Effect of water coagulation bath temperature*

The solvent and non-solvent exchange rate is a key factor that determines the final membrane morphology. As mentioned previously for the lab-scale results, a faster exchange rate resulted in a larger pore size and a higher porosity at a higher coagulation bath temperature. As shown in Table 4, the pore size increased from 67.5 to 77.5 nm by elevating the bath temperature from 26 to 30 °C for the 12.5 wt% polymer casting solution. Similarly, both the surface pore size and porosity increased at a higher temperature for 13 wt% and 14 wt% polymer casting solutions as shown in the same table. The porosity increased gradually at higher temperatures as well, as exhibited in the SEM images in Fig. 10. In addition, this figure illustrates the corresponding SEM images of surface morphologies with different water coagulation bath temperatures that are summarized in Table 4. Therefore, it could be pointed out that the water bath temperature is a crucial parameter for defining the final morphology of the PES membrane in pilot-scale fabrication. Figs. 7 and 10 and Table 4 have shown the effect of coagulation bath temperature on the surface morphologies in both lab-scale and pilot-scale membranes, respectively. Changing the temperature from 25 °C to 30 °C increased the average pore size from 67.5 nm to 77.5 nm for pilot-scale membranes, whereas only a small change was observed for the lab-scale membranes. It can be concluded that the significance of temperature in pilot-scale fabrication was much greater than that in lab-scale fabrication, which was due to a higher solvent/non-solvent exchange rate associated with the pilot-scale fabrication that will be discussed thoroughly in Section 4.

Table 4. Effect of water coagulation bath temperature on the surface morphologies of pilot-scale PES membranes.

Membrane No.	PES con. (wt%)	2-ME/NMP	Casting solution temperature (°C)	Water coagulation bath (°C)	Pore size (nm)	Surface porosity (%)
M-7 I	12.5	60/35	20	25	67.5	16.8
M-7 II	12.5	60/35	20	26	68.9	16.9
M-7 III	12.5	60/35	20	28	71.9	17.4
M-7 IV	12.5	60/35	20	29	73.6	17.2
M-7 V	12.5	60/35	20	30	77.5	17.8
M-8 I	13	60/35	20	18	61.8	15.6
M-8 II	13	60/35	20	26	68.9	17.0
M-9 I	14	58/35	26	26	67.0	16.2
M-9 II	14	58/35	26	35	94.2	14.9

Fig. 10. SEM images demonstrating the effect of water coagulation bath temperature on the surface morphology of the pilot-scale PES membranes: a. M-7 I (25 °C); b. M-7 II (26 °C); c. M-7 III (28 °C); d. M-7 IV (29 °C); e. M-7 V (30 °C); f. M-8 I (18 °C); g. M-8 II (26 °C); h. M-9 I (26 °C); i. M-9 II (35 °C).

3.2.3. *Effect of PES layer thickness*

Compared to the observation that a higher thickness led to a less open morphology in the lab-scale PES membranes as shown in Fig. 8, the effect of the thickness was not significant in the pilot-scale membranes. Table 5 summarizes the surface morphologies of the pilot-scale membranes with different thicknesses. According to Table 5, the surface morphology barely changed from 20 μm to 30 μm for M-10, and 35 μm to 113 μm for M-11. Nevertheless, a

thickness difference beyond 30 μm caused a noteworthy variance on the lab-scale fabricated PES membranes as indicated in Fig. 8 in the previous section. The main reason for this difference was also due to the high solvent/non-solvent exchange during phase inversion in pilot-scale fabrication.

Table 5. Membrane morphologies of the pilot-scale PES membranes with different thicknesses.

Membrane No.	PES layer thickness (μm)	Pore size (nm)	Porosity (%)
M-10 I ^a	30	61.8	15.6
M-10 II ^a	20	61.9	15.6
M-11 I ^b	113	52.5	11.9
M-11 II ^b	35	52.7	12.0

❖ ^a PES: 13wt%, 2-ME/NMP: 60/35, humidity: 60%, exposure time: 6.25sec; water: 18 °C.

❖ ^b PES: 15wt%, 2-ME/NMP: 56/35, humidity: 50%, exposure time: 2.5sec; water: 28 °C.

3.2.4. Gas transport properties of PES membranes

The gas permeation resistance of a multi-layer composite membrane comprises the resistances from both the top selective layer and the substrate [44]. Peinemann and Pinnau reported that the support layer affected the total gas permeation rate significantly in a composite membrane [45]. The support resistance, which is determined by the morphology of the support, is an important factor for the CO₂ transport property in composite membrane. More open morphology leads to a lower resistance, which increases the CO₂ permeance for membranes used in CO₂ capture. The resistance from the non-woven fabric was neglected as it showed a CO₂ permeance of ~ 32000 GPU (gas permeation unit, $1 \text{ GPU} = 10^{-6} \text{ cm}^3(\text{STP})/(\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg})$) and a CO₂/N₂ selectivity of 0.88. Fig. 11 shows the gas transport property of the PES membranes with different pore sizes. As shown, PES membrane with a larger pore size, potentially a lower resistance, exhibited a higher CO₂ permeance than a smaller pore size PES. Since Knudsen

diffusion is dominant for gas molecules transport through a nanoporous PES membrane, the selectivity of CO_2/N_2 equals to the reciprocal square root of their molecular weights, which is ~ 0.8 [46]. The observed average selectivity of 0.87 in our study was in a good agreement with the theoretical value. Moreover, the gas molecules could collide with the pore walls less frequently in the PES membrane with bigger pore diameter. As a result, both CO_2 and N_2 molecules could transport more easily through a PES with bigger pores, leading to a decrease of CO_2/N_2 selectivity as observed in Fig. 11. Based on the resistance-in-series model for composite membranes [44], with assumption that the CO_2 permeance of the PES layer is 8500 GPU, the PES layer provides over 10% of the total resistance of the composite membrane when the selective layer permeance is higher than 950 GPU. This indicates the importance of an open morphology with less resistance in order to improve the performance of the composite membrane.

Fig. 11. Gas transport property of PES membranes with different pore sizes.*

* The corresponding surface porosity values of the three PES membranes were 11.3%, 17.0%, and 17.8%, respectively.

3.2.5. Gas transport performances of the composite membrane

A selective layer was coated on PES membranes (supports) with various pore sizes as shown in Fig. 11. The final composite membranes were tested under the same conditions as the PES membranes. Table 6 summarizes the transport performances of the composite membranes. Fig. 12 shows the cross-sections of the composite membranes, and the thicknesses of the selective layers are listed in Table 6, indicating a similar thickness for the three membranes. The more detailed characterization of the selective layer can be found in [33]. As shown in Table 6, because of the smaller pore size and lower porosity, the high mass transfer resistance for the PES support with a pore size of ~ 42.2 nm reduced the final transport performance of the composite membrane. Although less resistance was obtained in the PES substrate with a bigger pore size, the penetration of the selective layer was introduced during coating due to the bigger pores. As a result, the composite membrane coated on the PES support with a pore size of ~ 77.5 nm showed a lower permeance than the composite membrane coated on the PES support with a pore size of ~ 69 nm. Therefore, the optimization of the substrate morphology was necessary for achieving a high gas permeation property.

Table 6. Transport performances of the composite membranes with different PES substrates.

PES average pore size (nm)	PES surface porosity (%)	Selective layer thickness (nm)	CO ₂ permeance (GPU)	CO ₂ /N ₂ selectivity
42.2	11.3	145	654	154
69	17.0	160	780	135
77.5	17.8	155	764	113

Fig. 12. Cross sections of the composite membranes with different PES substrates: a. PES pore size of 42.2 nm; b. PES pore size of 69 nm; c. PES pore size of 77.5 nm.

4. Discussion

4.1 Morphological differences between lab-scale and pilot-scale membranes

The same preparation conditions were used for both lab-scale and pilot-scale membranes. However, obvious surface morphology differences were observed for the membranes fabricated in different scales. The SEM images in Fig. 13 show the surface morphologies of the PES membranes from both scales, and Table 7 summarizes the corresponding average pore size and surface porosity results. As shown in this figure and this table, the PES membranes fabricated in

the pilot scale had a much larger pore size and a higher porosity than the lab-scale membranes by applying the same preparation conditions.

The immersion step in the non-solvent that induced phase inversion was a key step in forming the final membrane structure since the solvent and non-solvent exchange occurred in this stage. The main differences of the immersion steps between the lab scale and pilot scale lay in the stationary and moving non-woven fabric inside of the coagulation bath, as well as the existence and absence of the non-porous glass plate, respectively. Above all, solvent diffused out at the interface between the cast film and the coagulant. Although the miscibility of solvent and non-solvent was good, the local solvent concentration at the interface in pilot scale was lower due to the moving web. Therefore, the demixing in lab scale was slower than that in pilot scale, leading to a less porous surface structure in lab-scale PES membranes.

In addition, without the glass plate as the barrier in the pilot scale, the solvent and non-solvent exchange occurred on both front and back sides of the cast film, which led to a faster phase inversion rate. Therefore, we believe that the water flux that caused phase separation in the immersion step was higher in the pilot scale than in the lab scale with the same residence time in the coagulation bath. This assumption can be demonstrated in the following simplified diffusion model.

Fig. 13. Surface morphologies of the lab- and pilot-scale membranes: a. L-M-1 ^a; b. P-M-1 ^a; c. L-M-2 ^b; d. P-M-2 ^b.

- ❖ L-M-1 and L-M-2 were lab-scale PES membranes, whereas P-M-1 and P-M-2 were pilot-scale PES membranes.
- ❖ ^a PES: 12.5 wt%, 2-ME/NMP: 58/35, humidity: 60%, exposure time: 6.25 sec, water: 55 °C.
- ❖ ^b PES: 12.5 wt%, 2-ME/NMP: 58/35, humidity: 60%, exposure time: 6.25 sec, water: 26 °C.

Table 7. Summary of the surface morphology analyses in Fig. 13.

Membrane No.	Pore size (nm)	Surface porosity (%)
L-M-1 ^a	54.8	14.1
P-M-1 ^a	110.7	14.6
L-M-2 ^b	30.1	11.4
P-M-2 ^b	68.7	16.1

❖ L-M-1 and L-M-2 were lab-scale PES membranes, whereas P-M-1 and P-M-2 were pilot-scale PES membranes.

❖ ^a PES: 12.5 wt%, 2-ME/NMP: 58/35, humidity: 60%, exposure time: 6.25 sec, water: 55 °C.

❖ ^b PES: 12.5 wt%, 2-ME/NMP: 58/35, humidity: 60%, exposure time: 6.25 sec, water: 26 °C.

4.2 Diffusion model for the solvent/non-solvent exchange at the first instance of immersion

After immersing in the coagulation bath, the polymer in the cast film solidifies with a simultaneous diffusion of solvent and non-solvent. The interface between the wet film and the coagulation bath containing non-solvent governs the surface and bulk morphologies of the membrane. The entire process is controlled by the solvent and non-solvent fluxes at the interface since the polymer is confined within the membrane [47]. Because of the exchange of the solvent and non-solvent between the **cast film** and the coagulation bath, the interface between them is not stationary [48]. Even though a moving boundary has been incorporated by many researchers in order to analyze the diffusion during the phase inversion [47–49], the flux at the first instance is still of greater importance to account for the morphological consequence. Therefore, for the simplified diffusion model in this study, the following flux equations only consider the non-solvent fluxes on the bath sides of the cast film at the first instance of immersion. We make the following assumptions to simplify the diffusion model:

- Polymer concentration is negligible in the water coagulation bath, therefore, only the diffusion of water, NMP and 2-ME are considered on the bath side.
- The composition at the interface between the wet film and the water bath is considered as a constant since the volume of the coagulation bath is much larger than the cast film. The bath is assumed to be well stirred.
- The boundary layer is much smaller than the cast film thickness.
- The non-woven fabric provides additional resistances for the transport of the solvent and the non-solvent. The additional resistance factor for the transport of the non-solvent is δ .

For the lab scale, the solvent and non-solvent exchange only occurred at the top interface between the **cast film** and the coagulation bath during quenching as illustrated in Fig. 14-a. The non-solvent (water) only diffused into the **cast film** through the top interface. Therefore, the water flux at the interface on the bath side for the lab-scale membrane is [18,48]:

$$J_1 = -\sum_{i=1}^3 L_{i1} \nabla \mu_1 \quad (1)$$

where J_1 and L_{ij} are the molar flux of water and the phenomenological coefficients related to the interface at the first instance of immersion, respectively. In the notation, 1, 2 and 3 are water, 2-ME, and NMP, respectively. μ_1 is the chemical potential of water at the first instance of immersion.

However, for the pilot-scale, an additional solvent and non-solvent exchange interface existed since the highly porous hydrophilic non-woven fabric was the only barrier separating the cast film from the coagulation bath instead of the glass plate, as shown in **Fig. 14-b**. It should be noted that the water flux at the top and bottom interfaces might be different because the non-woven fabric provided an extra mass transfer resistance for water. Such an effect was considered

by a resistance factor δ . Therefore, the total interfacial water flux on the bath side for the pilot-scale is:

$$J'_1 = -\sum_{i=1}^3 [L_{i1} + (L_{i1} - \delta L_{i1})] \nabla \mu_1 \quad (2)$$

where δ is the resistance factor of the non-woven fabric.

Fig. 14. Schematic representation of the interface between the cast PES film and the water coagulation bath during the immersion precipitation process in: a. lab scale; b. pilot scale.

It is reasonable to assume that the non-woven fabric resistance factor δ is close to 0 if its resistance is extremely low and it is naturally hydrophilic. As a result, $J'_1 \sim 2 J_1$, which causes the significant morphology difference in the two scales. Specially, a larger non-solvent flux associated with instantaneous phase separation resulted in a very steep surface polymer concentration profile [47]. A steep polymer concentration profile at the interface during immersion could induce a fingering structure formation associated with a higher porosity. However, the addition of the non-solvent (2-ME) in the casting solution could accelerate the phase separation, which resulted in a highly spongy structure in the bulk of the membrane [4,37,38]. As a result, the coupling effect of those two factors led to a more porous surface as well as a spongy bulk layer. In addition, the lower non-solvent flux in the lab scale was similar

to the case of adding solvent in the coagulation bath, resulting in a longer precipitation time and a smoother polymer profile [47,50]. Consequently, a denser skin layer with fewer pores and lower porosity was formed in the lab scale, which was in line with our hypothesis and observations.

Both the lab-scale and pilot-scale PES membranes were peeled off carefully from the non-woven fabric and then observed via SEM. Though the fabric provided a resistance for the solvent/non-solvent exchange compared to the front side, unlike the dense bottom layer on the backside for the lab-scale PES membranes [49], a highly porous bottom layer was formed for the pilot-scale PES membranes as shown in Fig. 15. According to Fig. 15-c and d, compared to the average pore sizes in the front side of P-M-1 and P-M-2 (68.7 and 110.7 nm, respectively), the average pore sizes on the bottom side of P-M-1 and P-M-2 were 1350 and 475 nm, respectively. It was evident that much bigger pores were formed in the skin layer on the bottom side compared to the front side. With the same time in the humidity chamber for the front and back (bottom) sides, a less number of nuclei were introduced on the backside of the PES membrane because of the gas resistance of the fabric to the transport of non-solvent water vapor. With the less number of nuclei on the back side, they could grow into much bigger pores with the similar non-solvent flux after immersion into the water bath because the pore walls solidified more slowly, i.e., for a longer time [51]. As a result, this second porous skin layer reduced the resistance of the PES membrane as a support layer for gas separation, which could improve the gas transport performance.

Fig. 15. SEM images of the backsides of the lab- and pilot-scale PES membranes: a. L-M-1 ^a; b. L-M-2 ^b; c. P-M-1 ^a; d. P-M-2 ^b.

- ❖ L-M-1 and L-M-2 were lab-scale PES membranes, whereas P-M-1 and P-M-2 were pilot-scale PES membranes.
- ❖ ^a PES: 12.5 wt%, 2-ME/NMP: 58/35, humidity: 60%, exposure time: 6.25 sec, water: 55 °C.
- ❖ ^b PES: 12.5 wt%, 2-ME/NMP: 58/35, humidity: 60%, exposure time: 6.25 sec, water: 26 °C.

With the two-side flux model, it could be concluded that the reason why the temperature effect was more significant and the thickness effect was less prominent on the surface morphology for the pilot scale than the lab scale was the non-solvent flux from two sides for the

pilot scale. As the temperature affected the kinetics of the solvent/non-solvent exchange, the effect of the temperature on the surface morphology was stronger in the pilot-scale PES membrane due to the higher non-solvent flux. Therefore, adjusting coagulation bath temperature was the major way to obtain a desired morphology. In addition, as the exchange in the immersion step determined the membrane morphology, the high non-solvent flux assured the non-solvent flux even for the case that the membrane was thick. As result, the thickness effect was less significant for pilot-scale PES membranes than for lab-scale membranes.

5. Conclusions

An open morphology, or a low resistance, was required for the PES membrane used as the support in composite membranes for gas separation. The two successive steps of VIPI followed by NIPI, as the widely used asymmetric membrane preparation technique, were applied in our study. In order to optimize the surface morphology, a detailed study of the preparation parameters in the lab scale was conducted. In addition, the process was translated into a pilot-scale fabrication for the production of 14-inch wide PES membrane with a controllable surface morphology.

In the lab-scale study, different operating parameters were examined, which provided guidelines for the fabrication of the pilot-scale PES membranes. Increasing 2-ME/NMP ratio, relative humidity, exposure time, and water coagulation bath temperature generally resulted in a larger pore size and a greater surface porosity. On the other hand, increasing polymer concentration and PES layer thickness led to a smaller pore size and a lower porosity.

In the pilot-scale fabrication, two changeable parameters, casting solution composition and water coagulation bath temperature, were studied thoroughly. Lowering polymer concentration and elevating water coagulation bath temperature increased pore size and surface porosity. As

non-solvent flux was crucial for determining the final membrane morphology, the simplified diffusion model indicated that the non-solvent flux of the pilot scale during the immersion precipitation stage was almost twice than that of the lab scale because of the absence of the non-porous glass plate. Therefore, the observations in this study showed that the surface morphology was more open in pilot-scale PES membranes than in lab-scale PES membranes with the same preparation conditions. In addition, the water coagulation bath temperature effect was more pronounced in pilot scale than in lab scale as the temperature affected the solvent/non-solvent exchange rate, which was the most important factor defining the final surface morphology of the PES membrane. On the contrary to the strong thickness effect for the lab-scale membranes, its effect was less significant in the pilot-scale membranes, which was also due to the high non-solvent flux during immersion precipitation in the water bath.

A suitable PES membrane with a desirable surface morphology was developed successfully. This study has shown the potential of this phase inversion process to be scaled up for large-scale PES membrane production.

Acknowledgments

We would like to thank José D. Figueroa of the National Energy Technology Laboratory and Yang Han for their helpful discussion and inputs and Yuanxin Chen for providing the selective layer coating solution. We would also like to thank BASF (Wyandotte, MI) for their free samples of the polyethersulfone materials and helpful discussion. We gratefully acknowledge the Department of Energy/National Energy Technology Laboratory (DE-FE007632) and the Ohio Development Services Agency (OOE-CDO-D-13-05) for their financial support of this work. This work was partly supported by the Department of Energy under Award Number DE-

FE0007632 with substantial involvement of the National Energy Technology Laboratory, Pittsburgh, PA, USA.

Nomenclatures

J_1 The molar flux of water at the first moment of immersion

L_{ij} Phenomenological coefficient relative to the interface that is between water, 2-ME, and

NMP

Greek letters

μ_1 The chemical potential of water at the first moment of immersion

δ The resistance factor of the non-woven fabric

References

- [1] W.S.W. Ho and K.K. Sirkar, eds., Membrane Handbook, Chapman & Hall, New York (1992), Kluwer Academic Publishers, Boston, reprint edition (2001).
- [2] L. Zeman, G. Tkacik, Thermodynamic analysis of a membrane-forming system water/N-methyl-2-pyrrolidone/polyethersulfone, J. Membr. Sci. 36 (1988) 119–140.
- [3] L. Sidney, S. Srinivasa, High flow porous membranes for separating water from saline solutions, US Patent 3,133,132 (1964).
- [4] S.J. Shin, J.P. Kim, H.J. Kim, J.H. Jeon, B.R. Min, Preparation and characterization of polyethersulfone microfiltration membranes by a 2-methoxyethanol additive, Desalination 186 (2005) 1–10.
- [5] M. Mulder, Basic principles of membrane technology, Springer Science & Business Media, New York, 1996.
- [6] S.C. Pesek, W.J. Koros, Aqueous quenched asymmetric polysulfone hollow fibers prepared by dry/wet phase separation, J. Membr. Sci. 88 (1994) 1–19.
- [7] D. Wang, K. Li, W.K. Teo, Polyethersulfone hollow fiber gas separation membranes prepared from NMP/alcohol solvent systems, J. Membr. Sci. 115 (1996) 85–108.
- [8] G.R. Guillen, Y. Pan, M. Li, E.M.V. Hoek, Preparation and characterization of membranes formed by non-solvent induced phase separation: A review, Ind. Eng. Chem. Res, 50 (2011) 3798–3817.
- [9] Z. Xu, F.A. Qusay, Polyethersulfone (PES) hollow fiber ultrafiltration membranes prepared by PES/non-solvent/NMP solution, J. Membr. Sci. 233 (2004) 101–111.

- [10] C. Barth, M.C. Goncalves, A.T.N. Pires, J. Roeder, B.A. Wolf, Asymmetric polysulfone and polyethersulfone membranes: Effects of thermodynamic conditions during formation on their performance, *J. Membr. Sci.* 169 (2000) 287–299.
- [11] D. Wang, K. Li, W.K. Teo, Relationship between mass ratio of non-solvent additive to solvent in membrane casting solution and its coagulation value, *J. Membr. Sci.* 98 (1995) 233–240.
- [12] J. Li, Z. Xu, H. Yang, Microporous polyethersulfone membranes prepared under the combined precipitation conditions with non-solvent additives, *Polym. Adv. Technol.* 19 (2008) 251–257.
- [13] H. Caquineau, P. Menut, A. Deratani, C. Dupuy, Influence of the relative humidity on film formation by vapor induced phase separation, *Polym. Eng. Sci.* 43 (2003) 798–808.
- [14] H.A. Tsai, C.Y. Kuo, J.H. Lin, D.M. Wang, A. Deratani, C. Pochat-Bohatier, K.R. Lee, J.Y. Lai, Morphology control of polysulfone hollow fiber membranes via water vapor induced phase separation, *J. Membr. Sci.* 278 (2006) 390–400.
- [15] J.S. Kang, K.Y. Kim, Y.M. Lee, Preparation of microporous chlorinated poly(vinyl chloride) membrane in fabric and the characterization of their pore sizes and pore-size distributions, *J. Appl. Polym. Sci.* 86 (2002) 1195–1202.
- [16] J.S. Kang, K.Y. Kim, Y.M. Lee, Preparation of PVP immobilized microporous chlorinated polyvinyl chloride membranes on fabric and their hydraulic permeation behavior, *J. Membr. Sci.* 214 (2003) 311–321.
- [17] M.G. Buonomenna, P. Macchi, M. Davoli, E. Drioli, Poly(vinylidene fluoride) membranes by phase inversion: The role the casting and coagulation conditions play in their morphology, crystalline structure and properties, *Eur. Polym. J.* 43 (2007) 1557–1572.

- [18] R.M. Boom, I.M. Wienk, Th. van den Boomgaard, C.A. Smolders, Microstructures in phase inversion membranes. Part 2. The role of a polymeric additive, *J. Membr. Sci.* 73 (1992) 277–292.
- [19] H. Lin, Z. He, Z. Sun, J. Vu, A. Ng, M. Mohammed, J. Knief, T.C. Merkel, T. Wu, R.C. Lambrecht, CO₂-selective membranes for hydrogen production and CO₂ capture – Part I: Membrane development, *J. Membr. Sci.* 457 (2014) 149–161.
- [20] K. Ramasubramanian, Y. Zhao, W.S.W. Ho, CO₂ capture and H₂ purification: Prospects for CO₂-selective membrane processes, *AIChE J.* 59 (2013) 1033–1045.
- [21] J. Huang, J. Zou, W.S.W. Ho, Carbon dioxide capture using a CO₂-selective facilitated transport membrane, *Ind. Eng. Chem. Res.* 47(2008) 1261–1267.
- [22] Y. Zhao, W.S.W. Ho, Steric hindrance effect on amine demonstrated in solid polymer membranes for CO₂ transport, *J. Membr. Sci.* 415 (2012) 132–138.
- [23] K. Ramasubramanian, H. Verweij, W.S.W. Ho, Membrane processes for carbon capture from coal-fired power plant flue gas: A modeling and cost study, *J. Membr. Sci.* 421 (2012) 299–310.
- [24] J. Zou, W.S.W. Ho, CO₂-selective polymeric membranes containing amines in crosslinked poly (vinyl alcohol), *J. Membr. Sci.* 286 (2006) 310–321.
- [25] Z. Qiao, Z. Wang, C. Zhang, S. Yuan, Y. Zhu, J. Wang, S. Wang, PVAm-PIP/PS composite membrane with high performance for CO₂/N₂ separation, *AIChE J.* 59 (2013) 215–228.
- [26] S. Yuan, Z. Wang, Z. Qiao, M. Wang, J. Wang, S. Wang, Improvement of CO₂/N₂ separation characteristics of polyvinylamine by modifying with ethylenediamine, *J. Membr. Sci.* 378 (2011) 425–437.

- [27] T.J. Kim, H. Vralstad, M. Sandru, M.B. Hägg, The effect of pH on CO₂-separation from post combustion gas by polyvinylamine based composite membrane, *Energy Procedia* 37 (2013) 986–992.
- [28] P. Li, H. Chen, T. Chung, The effects of substrate characteristics and pre-wetting agents on PAN–PDMS composite hollow fiber membranes for CO₂/N₂ and O₂/N₂ separation, *J. Membr. Sci.* 434 (2013) 18–25.
- [29] J.J. Shieh, T.S. Chung, Cellulose nitrate-based multilayer composite membranes for gas separation, *J. Membr. Sci.* 166 (2000) 259–269.
- [30] T.S. Chung, J.J. Shieh, W.Y. Lau, M.P. Srinivasan, D.R. Paul, Fabrication of multi-layer composite hollow fiber membranes for gas separation, *J. Membr. Sci.* 152 (1999) 221–225.
- [31] T.C. Merkel, H. Lin, X. Wei, R. Baker. Power plant post-combustion carbon dioxide capture: an opportunity for membranes, *J. Membr. Sci.* 359 (2010) 126–139.
- [32] I. Soroko, M. Makowski, F. Spill, A. Livingston, The effect of membrane formation parameters on performance of polyimide membranes for organic solvent nanofiltration (OSN). Part B: Analysis of evaporation step and the role of a co-solvent, *J. Membr. Sci.* 381 (2011) 163–171.
- [33] Y. Chen, L. Zhao, B. Wang, P. Dutta, W.S.W. Ho, Amine-containing polymer/zeolite-Y composite membranes for CO₂/N₂ separation, *J. Membr. Sci.* 497 (2016) 21–28.
- [34] H. Strathmann, K. Kock, The formation mechanism of phase inversion membranes, *Desalination* 21 (1977) 241–255.
- [35] D.B. Mosqueda-Jimenez, R.M. Narbaitz, T. Matsuura, G. Chowdhury, G. Pleizier, J.P. Santerre, Influence of processing conditions on the properties of ultrafiltration membranes, *J. Membr. Sci.* 231 (2004) 209–224.

- [36] C.A. Smolders, A.J. Reuvers, R.M. Boom, I.M. Wienk, Microstructures in phase-inversion membranes. Part 1. Formation of macrovoids, *J. Membr. Sci.* 73 (1992) 259–275.
- [37] J.Y. Lai, F.C. Lin, C.C. Wang, D.M. Wang, Effect of nonsolvent additives on the porosity and morphology of asymmetric TPX membranes, *J. Membr. Sci.* 118 (1996) 49–61.
- [38] T. Hou, S. Dong, L. Zheng, The study of mechanism of organic additives action in the polysulfone membrane casting solution, *Desalination* 83 (1991) 343–360.
- [39] L. Gao, B. Tang, P. Wu, An experimental investigation of evaporation time and the relative humidity on a novel positively charged ultrafiltration membrane via dry-wet phase inversion, *J. Membr. Sci.* 326 (2009) 168–177.
- [40] C. Yen, H. He, L.J. Lee, W.S.W. Ho, Synthesis and characterization of nanoporous polycaprolactone membranes via thermally- and nonsolvent-induced phase separations for biomedical device application, *J. Membr. Sci.* 343 (2009) 180–188.
- [41] M. Amirilargani, E. Saljoughi, T. Mohammadi, M.R. Moghbeli, Effects of coagulation bath temperature and polyvinylpyrrolidone content on flat sheet asymmetric polyethersulfone membranes, *Polym. Eng. Sci.* 50 (2010) 885–893.
- [42] M.A. Hajasgarkhani, S.M. Mousavi, E. Saljoughi, Effects of coagulation-bath temperature and montmorillonite nanoclay content on asymmetric cellulose acetate butyrate membranes, *Clays Clay Minerals* 61 (2013) 541–550.
- [43] D. Li, T.S. Chung, J. Ren, R. Wang, Thickness dependence of macrovoid evolution in wet phase-inversion asymmetric membranes, *Ind. Eng. Chem. Res.* 43 (2004) 1553–1556.
- [44] J.M.S. Henis, M.K. Tripodi, Composite hollow fiber membranes for gas separation: The resistance model approach, *J. Membr. Sci.* 8 (1981) 233–246.

- [45] K.V. Peinemann, I. Pinnau, Method for producing an integral asymmetric gas separation membrane and the resultant membrane, US Patent 4,746,333 (1988).
- [46] W.M. Deen, Analysis of Transport Phenomena, Oxford University Press, New York, 2011.
- [47] L.P. Cheng, Y.S. Soh, A.H. Dwan, C.C. Gryte, An improved model for mass transfer during the formation of polymeric membranes by the immersion-precipitation process, J. Polym. Sci. Part B: Polym. Phys. 32 (1994) 1413–1425.
- [48] A.J. Reuvers, J.W.A. van den Berg, C.A. Smolders, Formation of membranes by means of immersion precipitation: Part I. A model to describe mass transfer during immersion precipitation, J. Membr. Sci. 34 (1987) 45–65.
- [49] C. Cohen, G.B. Tanny, S. Prager, Diffusion-controlled formation of porous structures in ternary polymer systems, J. Polym. Sci.: Polym. Phys. Ed. 17 (1979) 477–489.
- [50] C.S. Tsay, A.J. McHugh, Mass transfer modeling of asymmetric membrane formation by phase inversion, J. Polym. Sci. Part B: Polym. Phys. 28 (1990) 1327–1365.
- [51] T.H. Young, L.W. Chen, Pore formation mechanism of membranes from phase inversion process, Desalination 103 (1996) 233–247.