

The Influence of Membrane Formation Parameters on Structural Morphology and Performance of PES/PDMS Composite Membrane for Gas Separation

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ABSTRACT: In this study, influence of membrane preparation parameters on structural morphology and performance of polyethersulfone/polydimethylsiloxane (PES/PDMS) composite membrane was investigated for gas separation. Asymmetric PES flat sheet membranes were composed by phase inversion method and used as supports. PES composite membranes were fabricated by coating silicone rubber as selective layer on the top surface of support. Effects of different concentrations of PES and PDMS, solvent type, and support thickness on membrane performance were investigated for separation of oxygen from nitrogen. The optimized superior membrane was further modified using polyvinylidene fluoride, methanol and ethanol as additives in PES solutions and/or in water coagula-

tion bath to promote the membrane capability. The results showed that addition of ethanol and methanol in cast solution and coagulation bath can greatly affect the morphology and hence the performance of the prepared membranes. The permeance changes have the contrary trend with solubility parameter difference between solvent and nonsolvent mixture, for instance when this parameter difference was lowest, higher permeance was obtained. Support and coating polymer concentration can control the permeance. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 827–839, 2011

Key words: membrane; PDMS; PVDF; additives; gas separation

INTRODUCTION

Polymers are primary materials for preparation of membranes with solution-diffusion mechanism. According to this three-step solution-diffusion mechanism, the gas first sorbs into the membrane on the high-pressure side, then diffuses across the membrane under a partial pressure driving force and finally, desorbs from the low-pressure side of the membrane. Therefore, gas permeability in the membrane is dependent both on the solubility of the gas in the polymer as well as its diffusion coefficient in the polymer. Gas solubility in polymers typically increases with increasing in gas condensability, in the absence of specific interactions between the gas molecules and the polymer chains.^{1,2} Increasing penetrant size decreases gas diffusion coefficients.² Thus, differences in molecular size and/or gas condensability can result in different gas permeation rates through a polymer.

For nonpolar gas mixtures, the separation is largely based on differences of molecular size. For similar-sized molecules like oxygen and nitrogen, rather limited permselectivities can be achieved.

Developing and improving membranes for increasing separation efficiency of O₂ from N₂ is one of the interesting fields for researchers. For this purpose, preparation and application capability of hollow fiber,^{3,4} flat sheet,^{5,6} and carbon molecular sieving (CMS)^{7,8} membranes were examined.

The phase separation process can be accomplished by a wide variety of techniques such as nonsolvent induced phase separation (NIPS), thermally induced phase separation (TIPS), vapor induced phase separation (VIPS), and evaporation induced phase separation (EIPS).⁹

Membranes that are prepared by the NIPS process usually contain large elongated voids (macrovoids) in their sublayer structure.¹⁰ The type and structure of these macrovoids has a large effect on the performance and mechanical strength of the resulting membranes. Several studies have been performed to discover the mechanism of macro void formation and to determine the effect of various parameters on the structure of the resulting macrovoids.^{10–13}

Asymmetric membrane has been widely used for gas separation and liquid separation. The thin top layer plays the role of a selective barrier and the porous sublayer, which includes macrovoids, pores and micropores, offers good mechanical strength.¹⁴ The capability of an asymmetric membrane to reject or admit a certain solute is, therefore, determined by the morphology, pore size, and pore density of the

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skin layer.¹⁵ The materials selection plays a vital role.¹⁶ To control the membrane structure, low molecular weight component is frequently used as additive in the membrane forming system.¹⁷

Rubbery membranes in general and polydimethylsiloxane (PDMS) in particular are superior choices for gas separations.¹⁸ The organophilic PDMS membranes have developed due to restricted environmental legislation.¹⁹

Recently, many studies have been carried out on transport properties of pure and binary gas mixtures of O₂, N₂, H₂, CO₂, CH₄, and C₂-C₄ paraffins and olefins using PDMS membranes.²⁰⁻³⁰ PDMS membranes which have been synthesized and evaluated in gas separation applications were in the form of a single layer,^{20,21} a composite with a microporous support,^{1,22-28} a mixed matrix,²⁹ and a copolymer.³⁰

The optimum gas separation membrane is obtained when the membrane combines a high selectivity with a high flux. The membrane materials and the membrane thickness determine the two basic properties. One method to minimize the membrane thickness is to prepare a composite membrane consisting of a thin film coated onto a microporous support.³¹ Most of PDMS composite membranes were prepared via casting PDMS solutions on microfiltration (MF) membranes such as polyamide (PA),²⁸ polypropylene (PP),³² polysulfone (PSf),^{25,33} polyvinylidene fluoride (PVDF),³⁴ and polyethersulfone (PES)^{1,24,35,36} to avoid intrusion of the organic casting solutions into the pores of the supports.

Sadrzadeh et al.^{1,36} synthesized a thin polydimethylsiloxane (PDMS) layer on polyethersulfone (PES) support and permeation of pure and mixed gases of C₃H₈, CO₂, CH₄, and H₂ were measured. They have investigated permeation behavior of the synthesized composite membrane gas experiments under various operating conditions and not discussed about effect of support structure on performance.

Wang et al.³⁵ have considered the gas permeation properties of H₂, He, CO₂, O₂, and N₂ through silicone-coated polyethersulfone asymmetric hollow-fiber membranes with different structures were investigated as a function of pressure and temperature and compared with PES dense and silicone rubber (PDMS) membranes.

In a previous work,²⁴ we used composite membranes for separation of ethylene from nitrogen using polyethersulfone as support and PDMS as active layer at various concentrations.

The main aim of the present study was investigation of support structure effect on performance of coated PDMS membrane for gas separation. For this reason, the structures of PES membranes consisting of different solvents and additives were investigated. This includes the addition of alcohols and PVDF in the casting solution and introducing alcoholic addi-

tives to the coagulation bath. Also, effect of support polymer concentration and active layer concentration on performance was considered.

EXPERIMENTAL

Materials

Polyethersulfone (PES) was supplied by BASF (Germany) and polydimethylsiloxane (PDMS) by Dow Corning (Midland, MI) were used as support and active layer of the composite membrane. PES was flake shape with molecular weight of 58,000, density of 1.37 g/cm³, and *T_g* of 225°C (data from BASF Company). Dimethylsulfoxide (DMSO) (98%), *N*-methylpyrrolidone (NMP) (99%), and dimethylformamide (DMF) (99.5%) were used as solvent for PES and *n*-hexane (99.9%) was employed as PDMS solvent. Ethanol and methanol were used as alcoholic additives. All solvents and additives were purchased from Merck, Germany.

PDMS (Sylgard 184 silicone elastomer kit) consists of two parts: polymer base and hardener. Polymer base (specific gravity 1.05 g/cm³ at 25°C, viscosity 5000 cSt) was a viscose and colorless liquid which has been consisted of dimethylsiloxane, dimethyl vinylterminated, dimethyl vinylated, and trimethylated silica as well as tetra (trimethylsiloxy) silane. Hardener (specific gravity 1.03 g/cm³ at 25°C, viscosity 110 cSt) was a nonviscose and colorless liquid consists of several compounds such as dimethyl methylhydrogen siloxane and tetramethyl tetravinyl cyclo-tetrasiloxane. The two parts were mixed together in a ratio of 10 : 1 (polymer base to hardener by wt %) suggested by supplier. PDMS was formed after curing in room temperature or oven.

Membrane preparation

Fabrication of support

Phase inversion method (PIM) was utilized for preparation of asymmetric support. Firstly PES was dried in oven at 110°C for 2 h to remove any traces of humidity. The dried PES was dissolved in solvents such as NMP, DMF, and DMSO with a specified concentration. When methanol and ethanol were used as additives, NMP was solvent. The solutions were mixed by magnetic stirrer for 12 h at room temperature.

Homogeneous solutions were cast on the glass plate by doctor blade that could adjust the film thicknesses. The casted films were dipped in water or water contained additives such as methanol or ethanol. The casting solutions were immediately coagulated. The prepared supports were immersed in water to remove the remaining solvent for 24 h. Finally, the membranes were placed between two

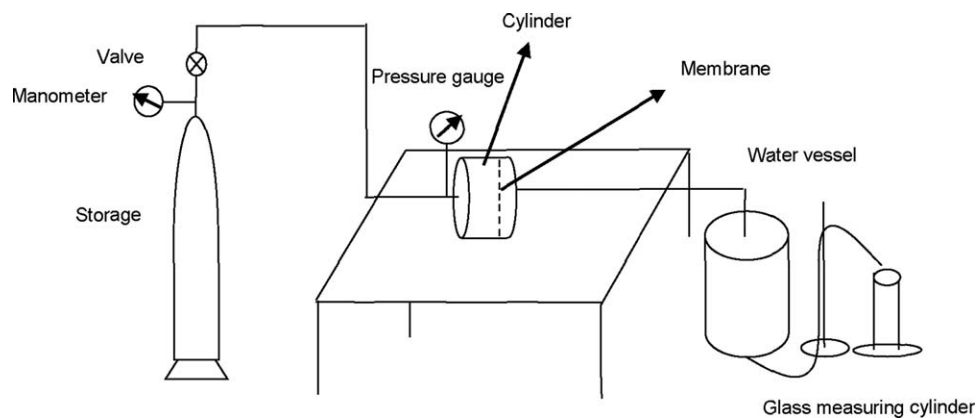


Figure 1 Experimental setup.

sheets of filter paper and dried for 24 h at room temperature. Solvent traces result in a brittle support with defects. The thicknesses of the supports were measured after coagulating and drying using micrometer

Composite membrane preparation

To prepare the coating solution, PDMS polymer base and hardener were mixed with the weight ratio of 10 to 1 and were added to a volatile solvent, *n*-hexane to obtain a homogeneous solution.

The support was coated with PDMS solution using a doctor blade with a thickness around 5 μm more than the support thickness to obtain a coating layer of 5 μm PDMS on sublayer. The solvent was completely evaporated during 24 h in an oven at 80°C.

Experimental setup

The experimental setup for measurement of nitrogen and oxygen permeability is described in Figure 1. The main part of the setup was a dead-end cell with diffusive disk chamber. The membrane was installed in the chamber as a disk with the effective area of 15.89 cm^2 . The applied pressure was in the range of 0.1 to 6 bar. The gases were supplied to the setup from compressed gas in storage. Oxygen and nitrogen permeability through the membrane was tested individually.

We employed a specifically designed instrument to obtain the permeance of gases. The gas permeate was conducted to a sealed vessel containing water. The quantity of flowed out water was measured in a specified time. This equals to the gas flow.

Flux was obtained on the basis of permeability as follows:

$$\frac{P}{l} = \frac{Q}{A\Delta p} \quad (1)$$

where P is permeability in $\text{cm}^3(\text{STP})\cdot\text{cm}/\text{cm}^2\cdot\text{sec}\cdot\text{cmHg}$, l is effective layer of separation in cm, Q is gas flow in $\text{cm}^3(\text{STP})/\text{s}$, A is effective membrane area in cm^2 and Δp is transmembrane pressure in cmHg.

Effective separation layer is unknown and therefore P/L (called permeance in $\text{GPU} = 1 \times 10^{-6} \text{cm}^3(\text{STP})/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$) is employed. Permeance is the normalized flux with pressure. Selectivity was defined as:

$$\alpha_{O_2/N_2} = \frac{(P/l)_{O_2}}{(P/l)_{N_2}} \quad (2)$$

Morphology evaluation

Cambridge Scanning Electron Microscope (SEM, CamScan MV2300) was used to investigate the morphology of the membranes. The samples were cut into the small pieces and cleaned with filter paper. The specimens were immersed in liquid nitrogen for 10 to 15 s and were frozen. The frozen membranes were broken and kept in air for drying. The dried samples were gold sputtered for producing electric conductivity. The micrographs were taken in high vacuum conditions at 27 kV. SEM images were obtained for cross section views of the polymeric membranes.

RESULTS AND DISCUSSIONS

Effect of support polymer concentration on gas separation

Membranes with 20, 25, and 30 wt % PES in NMP as casting solution were utilized to prepare support. The prepared layers were coated by 10 wt % PDMS. The thicknesses of support and coating layers were 60 and 5 μm , respectively. Oxygen and nitrogen permeance of the prepared membranes are shown in Figure 2. In 30 wt %, there was no permeance.

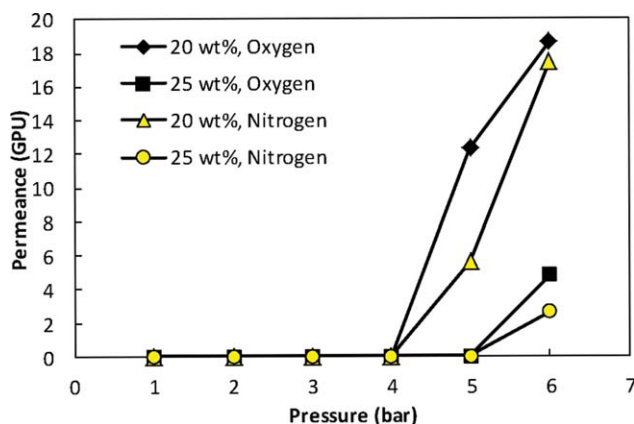


Figure 2 Effect of support polymer concentration on permeance (20, 25 and 30 wt % PES in NMP as solvent coated with 10 wt % PDMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, for 20 and 25 wt % concentrations of support layer, permeance was observed at moderate pressures of 5 and 6 bar. Selectivity was 2.2 and 1.07 for 20 wt % at 5 and 6 bar, respectively. For 25 wt % PES and 10 wt % PDMS, only at 6 bar permeance was detected with the selectivity of 1.82. The highly concentrated polymer that results in a tight structure, and/or low applied pressure, which means nonadequate driving force results in a membrane with no gas permeation. It is reported that increasing the concentration of polymer in casting solution suppress the formation of macrovoids in membrane prepared by the NIPS process^{11,12,37,38} leading to a decline in membrane permeability.

Effect of active layer concentration

On the basis of the preliminary results, further membranes were prepared with 20 wt % PES as the support backbone in NMP as solvent. The 60 μm support was coated by 3, 5, and 10 wt % PDMS. The thickness of the active layer was maintained at 5 μm . The effects of coating layer concentration are presented in Table I. By decreasing PDMS concentra-

tion, membrane permeance was improved. Moreover, permeability was observed at low pressure.

When mass concentration of the coating solution was enhanced, viscosity was increased and thereby evaporation time was enhanced. As a result, the coating layer on PES surface was denser led to permeance decline.³⁹ On the other hand, lower concentration of coating layer produces a low density coating with permeance at low pressures.

Influence of PES thickness as support layer

We investigated the thickness effect of 20 wt % PES dissolved in NMP. The supports with 60, 75, and 105 μm thicknesses were coated by 3 wt % PDMS. The permeances of oxygen and nitrogen and O_2/N_2 selectivity are presented in Table II. Permeance was decreased when support thickness was increased, with no remarkable changes in selectivity.

The flux was found to be inversely proportional to the membrane thickness but the selectivity remains nearly unaffected.³⁹ A decline in the thickness of the membrane support increases the performance. However, mechanical strength of the thinner membrane is the limiting factor.

With thicker membranes, higher pressure must be applied. However, higher selectivity was achieved at low applied pressure. Nitrogen requires higher pressure when encounter thicker coating. This is due to low solubility coefficient of nitrogen in PDMS compared with oxygen.²⁵ In other words nitrogen prefers to stay behind the PDMS matrix. In summary, the predominant mechanism at low pressure is solution with no pronounced effect of pressure. In this case the difference in solubility plays a vital role important role.

Effect of solvent type on morphology and performance

The gas transport properties of polymeric membranes depend on many factors including the solvent for membrane preparation. Solvents have

TABLE I
Effect of PDMS Concentration on Permeance (GPU) and Selectivity of the Prepared Membrane (20 wt% PES) in NMP as Solvent Coated with 10, 5, and 3 wt% PDMS

	1 bar		2 bar		3 bar		4 bar		5 bar		6 bar	
	O_2	N_2	O_2	N_2	O_2	N_2	O_2	N_2	O_2	N_2	O_2	N_2
Permeance (GPU)												
10%	—	—	—	—	—	—	—	—	12.3	5.6	18.6	17.5
5%	—	—	—	—	—	—	10.5	—	22.7	6.9	34.9	22.5
3%	5.8	—	15.8	7.4	21.4	11.8	26.2	16.1	27.9	21	31.7	25.2
Selectivity (O_2/N_2)												
10%	—	—	—	—	—	—	—	—	2.2	—	1.07	—
5%	—	—	—	—	—	—	∞	—	3.3	—	1.55	—
3%	∞	—	2.1	—	1.81	—	1.62	—	1.3	—	1.26	—

TABLE II
Influence of Support Layer Thickness on Permeance (GPU) and Selectivity of the Prepared Membrane (20 wt% PES) in NMP as Solvent Coated with 3 wt% PDMS

	1 bar		2 bar		3 bar		4 bar	
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
Permeance (GPU)								
60 (μm)	5.8	–	15.8	7.4	21.4	11.8	26.2	16.1
75 (μm)	2.8	–	16.7	5.7	18.6	11.5	24.5	15.2
105 (μm)	–	–	–	–	12.1	–	20.3	10.3
Selectivity (O ₂ /N ₂)								
60 (μm)	∞		2.1		1.8		1.62	
75 (μm)	∞		2.92		1.62		1.61	
105 (μm)	–		–		∞		1.95	

various chemical and physical properties which not only induce different interactions with polymer chains, but also result in different phase inversion processes during fabrication. Accordingly, membranes prepared by different solvents may have different morphologies and performance.⁴⁰

The membranes were prepared with 20 wt % PES as the support backbone in DMSO, DMF and NMP as solvent. The 60 μm support was coated by 3 wt % PDMS.

Cast solution properties are related to polymer concentrated solutions with many deficiencies existing among macromolecules due to interactions of molecular chains. More trouble would form on molecular chain of PES when the solvent with higher solubility and polarity parameter was used because of the stronger interaction between molecules of polymer and solvent. The solvent exchange process and the kinetics between the membrane and the quench bath possess a great influence on formation of desired macrovoids and controlled skin thickness.

The solubility parameter (δ_{sp}) and polarity parameter (δ_{pp}) of employed solvents⁴¹ are depicted in Table III. The solubility parameter (δ_{sp}) and polarity parameter (δ_{pp}) of DMSO are the highest within three different solvents. So more stress would be fixed between entanglements in the membranes prepared from the casting solution with DMSO as solvent and more shrinkage appears during drying process. Solubility parameter and polarity parameter of three different solvents were compared as follow, DMSO > DMF > NMP, and the shrinkage ratios of three membranes prepared from the casting solution with three different solvents also decrease in turn. It is suggested the higher solubility and polarity

TABLE III
Solubility and Polarity Parameter of the used Solvents

Solvent	DMSO	DMF	NMP
δ_{sp} (MPa ^{1/2})	26.7	24.8	22.9
δ_{pp} (MPa ^{1/2})	16.4	13.7	12.3

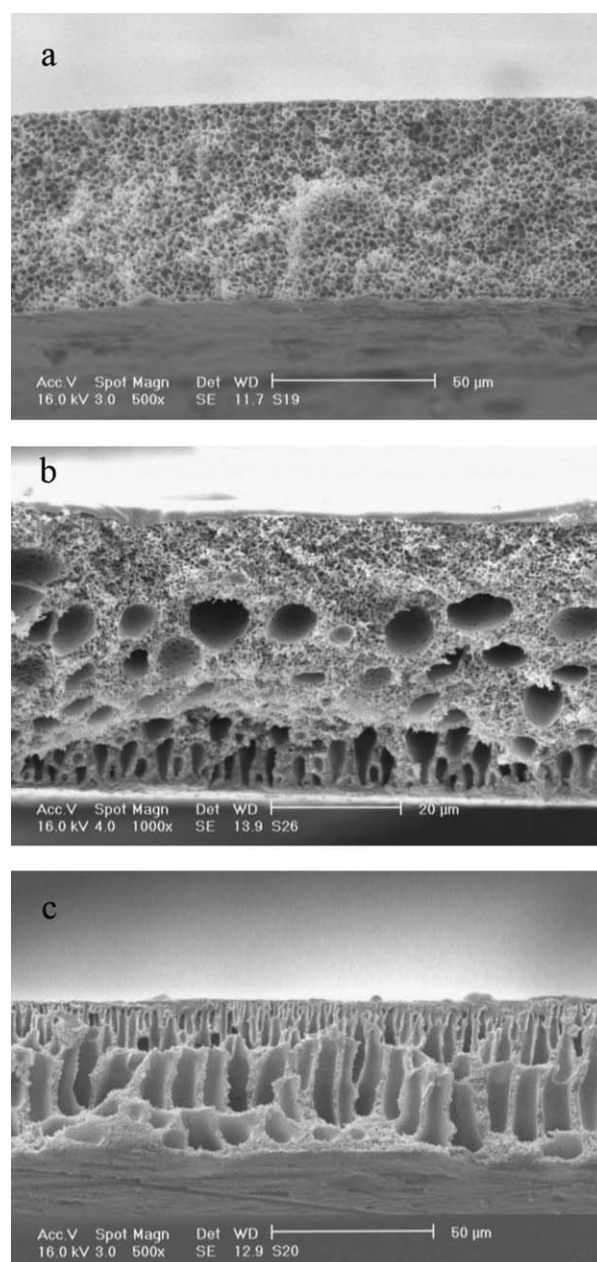


Figure 3 Cross-section SEM micrographs of the prepared membrane (20 wt % PES) in different solvents coated with 3 wt % PDMS (a) DMSO, (b) DMF, (c) NMP.

TABLE IV
Influence of Solvent Type on Permeance (GPU) and Selectivity of the Prepared Membrane (20 wt% PES) in NMP, DMF, and DMSO Coated with 3 wt% PDMS

Pressure	1 bar		2 bar		3 bar		4 bar		5 bar		6 bar	
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
Permeance (GPU)												
NMP	5.8	–	15.8	7.4	21.4	11.8	26.2	16.1	27.9	21	31.8	23.3
DMF	15.2	11	116	99.8	174	155	209.6	187.1	239.5	209.6	232.9	194.1
DMSO	–	–	72.27	64.4	116.4	116.4	174.6	149.7	167.6	139.2	174.6	139.7
Selectivity (O ₂ /N ₂)												
NMP	∞		2.13		1.81		1.63		1.33		1.36	
DMF	1.38		1.16		1.12		1.12		1.14		1.2	
DMSO	–		1.12		1		1.16		1.2		1.25	

parameters of solvent leads to higher shrinkage ratio of the prepared membrane.⁴²

As shown in Figure 3, sponge-like structure was obtained with DMSO as solvent. This is due to slow rate of membrane formation. Finger-like structure was produced at higher membrane formation rate i.e., using DMF and NMP.

DMF was utilized as solvent to prepare membranes having finger-like structure in less volume and remainder volume is sponge-like structure with some horizontal macrovoids, and the walls of finger-like pores are thicker, which indicates that membrane formation rate is slower than NMP. Many small finger-like pores and thicker skin layer formed in the membrane prepared from casting solution with NMP.

Oxygen and nitrogen were tested individually to know, which structure was more convenient for O₂/N₂ separation. Membranes fabricated by DMSO had high permeability but had no acceptable selectivity. Membranes prepared with NMP with finger-like structure and thicker skin layer, had lowest permeance and higher O₂/N₂ selectivity as shown in

Table IV. Accordingly we employed this solvent for continuation of the current research.

Effect of adding PVDF to PES casting solution

The addition of additives into a casting solution is an important method to modify membranes and achieve the desired properties. The permeances of previously fabricated membranes were low, and therefore we used PVDF as an additive in the casting solution.

The membrane support backbone was prepared with 20 wt % PES containing 1, 3, and 5 wt % polyvinylidene fluoride in NMP as solvent. The 60 μm support was coated by 3 wt % PDMS. Oxygen and nitrogen were permeated individually from these blend membranes. Permeance and selectivity are presented in Figures 4 and 5, respectively. In 5 wt % PVDF (not shown), the permeance was very high (898 and 1540 GPU for oxygen at 1 and 6 bar, respectively) and the selectivity was close to one. When PVDF was added to the casting solution, the permeance especially at low pressure was increased.

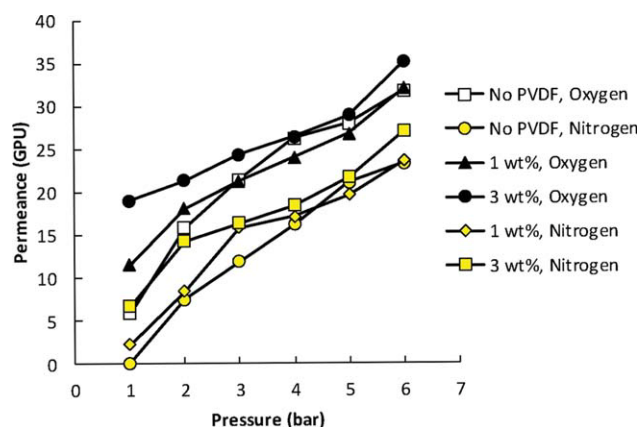


Figure 4 Influence of PVDF concentration as additive on permeance (20 wt % PES in NMP as solvent coated with 3 wt % PDMS). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

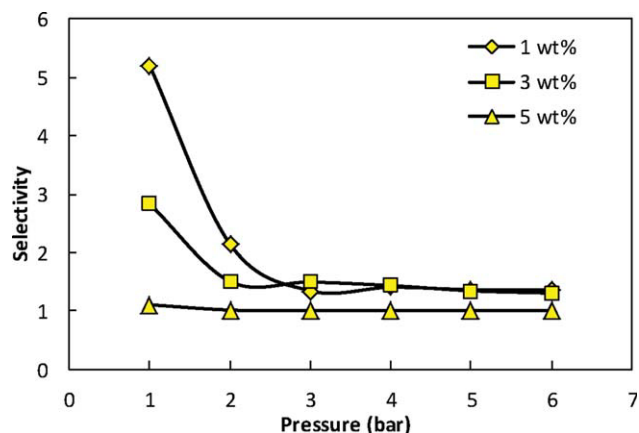


Figure 5 Influence of PVDF concentration as additive on selectivity (20 wt % PES in NMP as solvent coated with 3 wt % PDMS). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

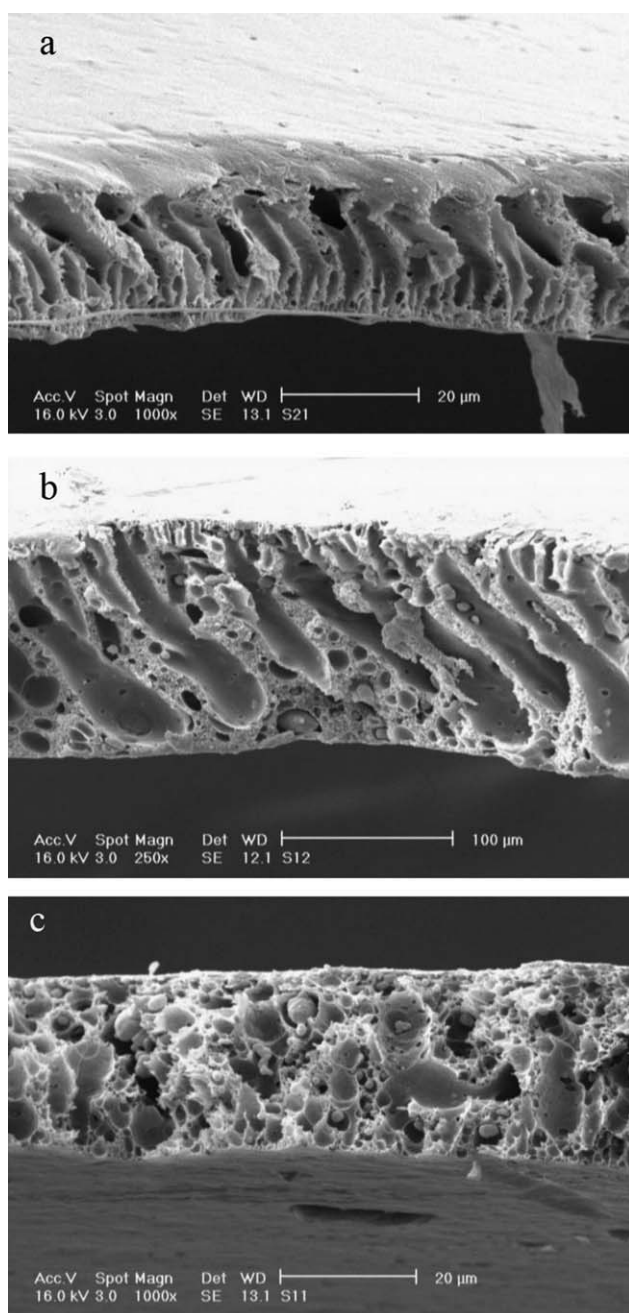


Figure 6 Cross-section SEM micrographs of the prepared membrane (20 wt % PES) with different concentrations of PVDF additives in NMP as solvent coated with 3 wt % PDMS (a) 1 wt % (b) 3 wt % (c) 5 wt %.

When PVDF concentration in casting solution was increased, macro void channels were enhanced and membrane structure was changed from finger-like structure to channel-like. This caused improved permeance. Selectivity at low pressure was enhanced. However, at high pressure it was not changed.

Solubility parameters of both polymers were considered to demonstrate the appearance of macro void channels that extend from up to bottom of structure as was shown in SEM Figure 6. It is postulated that the miscibility of blending polymers

depends on the difference of the solubility parameter of each polymer. The solubility parameter of PVDF and PES are 15.1 and 11.19 $(\text{cal}/\text{cm}^2)^{1/2}$, respectively,^{41,43} and the difference of both solubility parameters is $3.91(\text{cal}/\text{cm}^2)^{1/2}$, which makes PVDF and PES be thermodynamically incompatible system. At low concentration, PVDF forms a dispersed phase in uniform matrix of PES. Weak interactions between PVDF and PES chains lead to larger distance between the two kinds of chains, and results in larger distance between both phases.

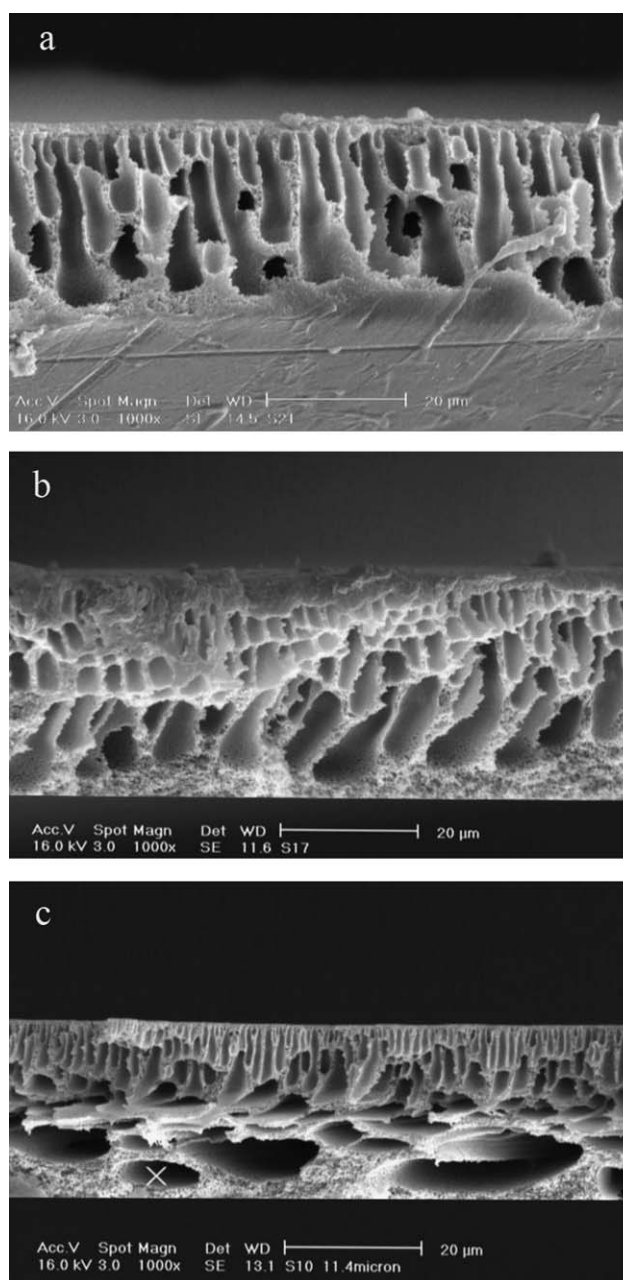


Figure 7 Cross-section SEM micrographs of the prepared membrane (20 wt % PES) with different concentrations of ethanol as additives in NMP as solvent coated with 3 wt % PDMS (a) 10 wt % (b) 15 wt % (c) 20 wt %.

TABLE V
Solubility Parameters of the Mixture of NMP/Nonsolvents and the Solubility Parameter Difference Between PES and NMP/Nonsolvents^{44,45}

Binary mixture of solvent and PES	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}	δ_t (MPa) ^{1/2}	Δ_{s-p} (MPa) ^{1/2}
NMP	18	12.3	7	22.9	2.03
EtOH	15.81	8.7	19.5	26.5	11.65
MOH	14.87	12.32	22.41	29.58	14.97
NMP/ EtOH 70 : 10	17.66	11.735	9.13	23.08	1.885
NMP/ EtOH 65 : 15	17.49	11.47	10.04	23.2	2.48
NMP/ EtOH 60 : 20	17.33	11.2	10.92	23.34	3.23
NMP/ MOH 70 : 10	17.5	12.3	12.49	24.77	5.06
NMP/ MOH 65 : 15	17.28	12.3	10.68	23.75	3.46
NMP/ MOH 60 : 20	17.06	12.3	11.76	24.48	4.42
PES	17.6	10.4	7.8	21.9	

Effect of adding ethanol and methanol to PES casting solution

The method of adding nonsolvent additive to improve the properties of the polymer membrane has been reported in the recent decade. Low molecular weight alcohol can be added as nonsolvent additive to enhance the porosity and permeability.^{44,45}

The membranes were prepared with 20 wt % PES as the support backbone, 10, 15, 20 wt % methanol and ethanol as additives in NMP as solvent. The 75 μm support was coated by 3 wt % PDMS. The thickness of the active layer was 5 μm .

Membranes without additives have long and wide finger-like structure extended from up to bottom side [Fig. 3(c)], while membrane with 10 wt % ethanol as additives (Fig. 7) have short and thin finger-like structure. In ethanol/NMP 15 : 65 wt %, finger-like structure was thinner and denser especially at top layer with macro voids at bottom side. Membrane structure with 20 wt % ethanol seems to change from finger-like to sponge-like structure as shown in Figure 7(c). In other words, the pore size of membrane is initially diminished with an increase in ethanol concentration in the dope solution. This is increased after ethanol concentration increases to

15 wt %. As a result, membrane morphology is slowly changed from long and wide finger-like structure through a thin finger-like structure to the sponge-like structure with some voids when ethanol concentration in the dope solution is increased. For description of these changes, the solubility parameters of binary solvent mixture should be considered.

The solubility parameter of a binary mixture (solvent/nonsolvent mixture and H₂O/alcoholic additives) is calculated based on the following equation^{46,47}:

$$\delta_{i,\Xi} = \frac{X_1 V_1 \delta_{i,1} + X_2 V_2 \delta_{i,2}}{X_1 V_1 + X_2 V_2}, i = d, p, h \quad (3)$$

where X is the molar fraction, V represents molar volume, and subscripts 1 and 2 refer to the solvent (NMP) and the nonsolvent additives when alcohols were added to casting solution and H₂O and alcoholic additives in coagulation bath mixture, respectively; subscripts d , p , and h represent dispersion, polar, and hydrogen bonding components of the solubility parameter of pure component, respectively.

The solubility parameter difference between PES and the binary solvent mixture and also between solvent and binary nonsolvent mixture can be calculated by

TABLE VI
Solubility Parameters of the Mixture of b) H₂O/Nonsolvents and the Solubility Parameter Difference Between NMP and H₂O/Nonsolvents^{44,45}

Binary mixture of H ₂ O and Nonsolvent	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}	δ_t (MPa) ^{1/2}	Δ_{s-N} (MPa) ^{1/2}
H ₂ O	15.87	15.5	42.39	47.84	35.4
EtOH	15.81	8.7	19.5	26.56	13
MOH	14.87	12.32	22.41	29.58	15.53
NMP/ EtOH 70 : 10	15.86	14.66	39.56	45.07	32.52
NMP/ EtOH 65 : 15	15.86	14.26	38.21	43.76	31.14
NMP/ EtOH 60 : 20	15.855	13.86	36.88	42.47	29.8
NMP/ MOH 70 : 10	15.31	13.73	31.29	37.44	24.28
NMP/ MOH 65 : 15	15.69	14.92	38.78	44.41	31.77
NMP/ MOH 60 : 20	15.63	14.74	37.63	43.33	30.62
NMP	18	12.3	7.2	22.9	2.03

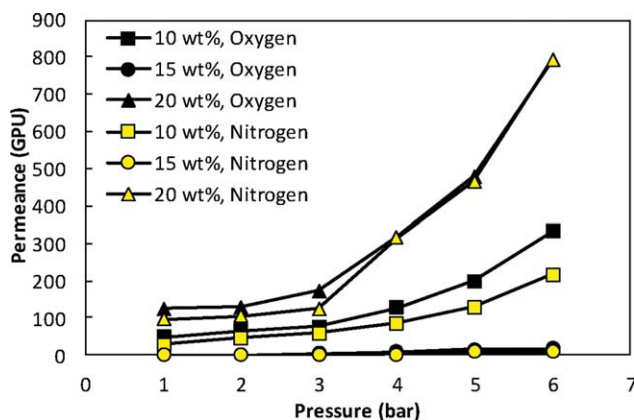


Figure 8 Influence of ethanol addition in casting solution on permeance of blend membrane (20 wt % PES) in NMP as solvent coated with 3 wt % PDMS (support layer 75 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

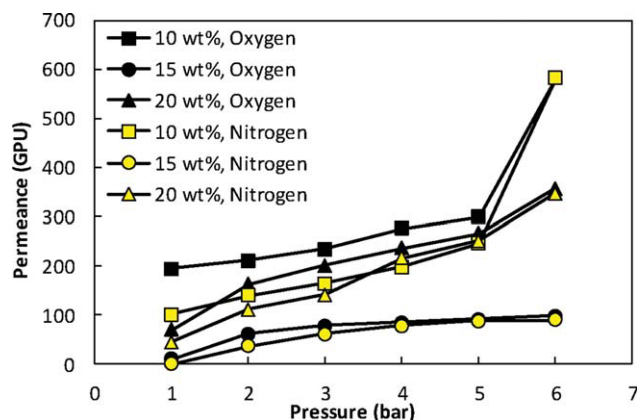


Figure 9 Influence of methanol addition in casting solution on permeance of blend membrane (20 wt % PES) in NMP as solvent coated with 3 wt % PDMS (support layer 75 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\delta_{s-i} = [(\delta_{d,s} - \delta_{d,p})^2 + (\delta_{p,s} - \delta_{p,p})^2 + (\delta_{h,s} - \delta_{h,p})^2]^{0.5}, \quad i = p, n \quad (4)$$

where $\delta_{i,p}$ represents the solubility parameter of PES.

Based on eqs. (3) and (4), solubility parameters of the mixture of NMP/nonsolvents and the solubility parameter difference between PES and NMP/nonsolvents are presented in Table V. The solubility parameter difference between NMP and H₂O/nonsolvents are calculated in Table VI.

Macrovoid channel-like structure is generally formed when coagulation process is fast, whereas the slow coagulation rate results in finger-like pores with thicker walls. If this rate becomes slower the sponge-like structure is obtained.^{17,45} The solubility parameter of binary mixture and solubility parameter difference between the polymer and the binary mixture (δ_i) increases with enhancing of ethanol concentration as shown in Table V and this cause to decrease the solubility parameter difference between solvent and nonsolvent and solubility of solvent to polymer as the result of more intense interaction of solvent with nonsolvent.^{48,49}

Figure 8 shows that permeance was increased with enhancing the ethanol concentration up to 10 wt % compared with membrane without additive. The permeance was severely reduced at 15 wt % and again extremely increased at 20 wt %. Although at 10 wt %, the pore size and finger-like width was reduced, permeance was increased. This may be due to the formation of thin PDMS layer on the membrane surface in this condition. Figure 9 and Table VII presented permeance and selectivity, respectively. The best selectivity was obtained at 15 wt % ethanol.

When the effect of adding methanol to casting solution was surveyed, different trends were encountered. The prepared membranes including methanol/NMP 10 : 70 wt % as solvent, have highest solubility parameter of binary mixture (δ_i) and solubility parameter difference between the polymer and binary mixture. The solubility parameter was initially decreased by increasing ethanol concentration to 15 wt % and again increased at 20 wt % of methanol/NMP. By increasing solubility parameter, the solvent can be removed faster and as shown in SEM images (Fig. 10), the dense layer changes to thinner and pores turn to interconnected leading to the permeance enhancement. In the case of 20 wt % methanol,

TABLE VII
Selectivity of the Prepared Blend Membrane 20 wt% PES and 10, 15, and 20 wt% of Ethanol or Methanol in NMP as Solvent Coated with 3 wt% PDMS (Support Layer 75 μm)

Pressure	1 bar	2 bar	3 bar	4 bar	5 bar	6 bar
(Selectivity (O ₂ /N ₂)-ethanol)						
10 wt%	1.65	1.44	1.28	1.46	1.55	1.5
15 wt%	–	–	∞	3	1.88	1.76
20 wt%	1.37	1.01	1.22	1	1.02	1
(Selectivity (O ₂ /N ₂)-methanol)						
10 wt%	1.93	1.51	1.43	1.39	1.21	1
15 wt%	∞	1.7	1.26	1.08	1.04	1.09
20 wt%	1.54	1.47	1.42	1.09	1.06	1.03

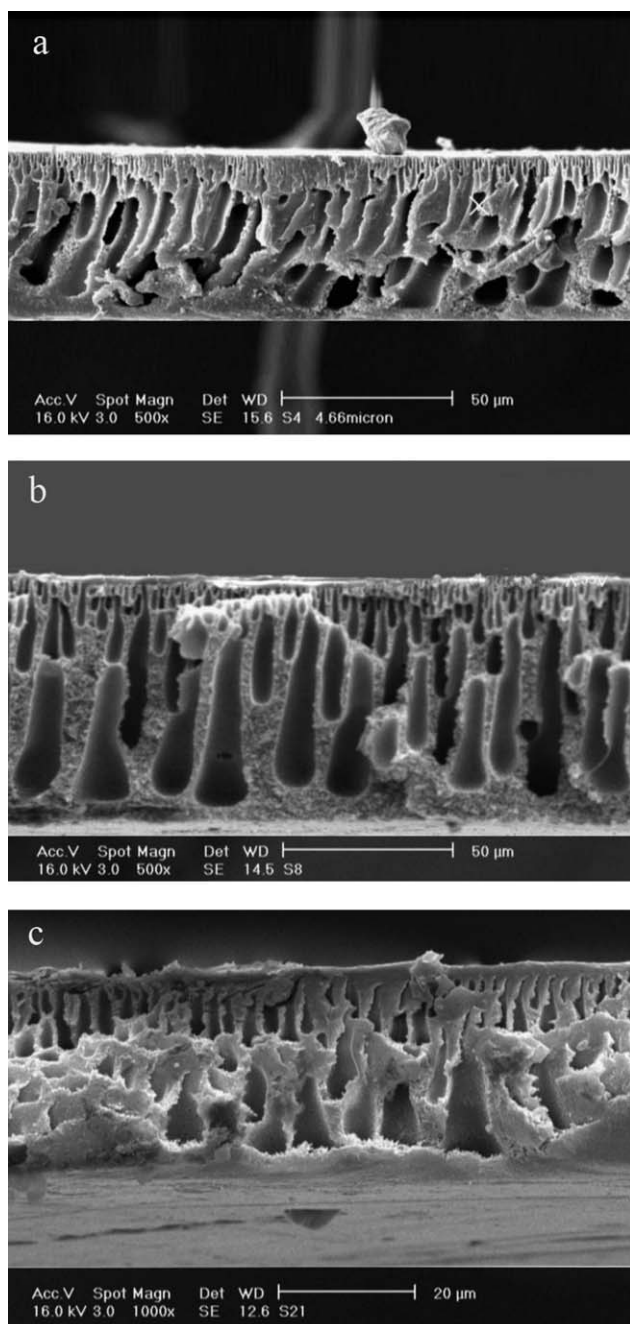


Figure 10 Cross-sectional SEM micrographs of prepared membrane (20 wt % PES) with different concentrations of methanol as additives in NMP as solvent coated with 3 wt % PDMS (a) 10 wt % (b) 15 wt % (c) 20 wt %.

the high permeance and the low selectivity value of the coated membrane, indicating that the defects (pores) were too large to be sealed with the silicone coating. The high permeance and no selectivity at 6 bar in 10 wt % methanol indicate the presence of large holes at high pressure.

Effect of adding ethanol and methanol to coagulation bath

The membranes were prepared with 20 wt % PES as the support backbone in NMP as solvent and were

soaked in 10, 15, 20 wt % methanol and ethanol as additives in water bath coagulation. The 75 μm support was coated by 3 wt % PDMS. The thickness of the active layer was 5 μm .

Solubility parameter of nonsolvent mixture and solubility parameter difference between solvent and nonsolvent decreased with increasing the ethanol concentration to nonsolvent bath (Table VI) and this cause to more interaction between solvent and binary nonsolvent mixture. Increasing exchange rate between solvent and nonsolvent led to more

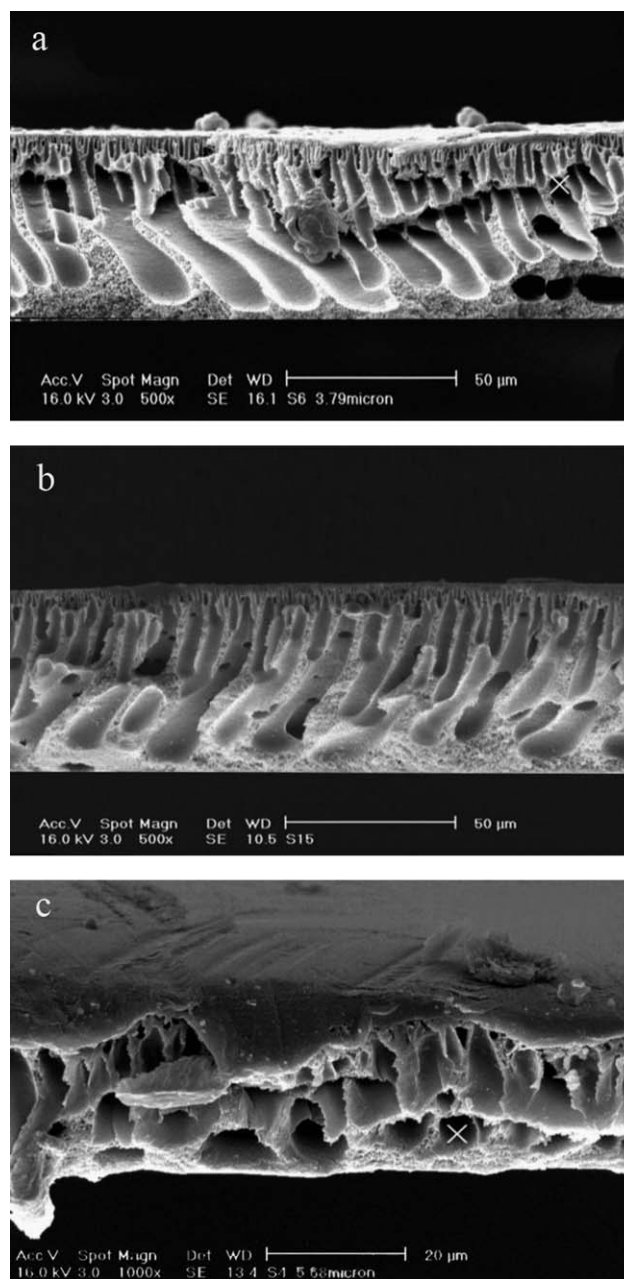


Figure 11 Cross-sectional SEM micrographs of the prepared membrane (20 wt % PES) in NMP as solvent, immersed in ethanol/ H_2O coagulation bath and coated with 3 wt % PDMS (a) 10/90 wt %, (b) 15/85 wt %, (c) 20/80 wt %.

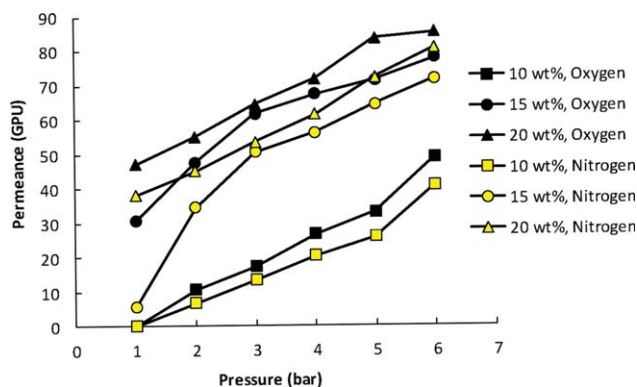


Figure 12 Influence of ethanol addition in coagulation bath solution on permeance of membrane (20 wt % PES) in NMP as solvent coated with 3 wt % PDMS (support layer 75 μ m). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interaction between solvent and binary nonsolvent mixture. This changed the dense layer to thinner with wider pores as shows in SEM images in Figure 11. Accordingly the permeance was increased as presented in Figure 12 and O_2/N_2 selectivity was decreased as shown in Table VIII.

The lowest solubility parameters of binary nonsolvent mixture of membranes coagulated in methanol/ H_2O 10 : 70 wt % compared with 15 and 20 wt % (see Table VI) results in higher interaction between solvent and nonsolvent leading to instantaneously removing solvent from membrane and creating the interconnected wide pores with thin dense layer (Fig. 13).

The solubility parameter of methanol/ H_2O mixture is initially increased with methanol concentration increment in coagulation bath and then increased after methanol concentration increment from 15 to 20 wt %. Due to highest solubility parameter of 15 wt % methanol concentration in bath coagulation, pores were not interconnected and thicker walls were formed. This was accompanied with formation of macrovoids in sublayer (sponge-like struc-

TABLE VIII
Selectivity of the Prepared Blend Membrane 20 wt% PES in NMP and 10, 15, and 20 wt% of Ethanol or Methanol as Additive in H_2O Coagulation Bath Coated with 3 wt% PDMS (Support Layer 75 μ m)

Pressure	1 bar	2 bar	3 bar	4 bar	5 bar	6 bar
Selectivity (O_2/N_2)-ethanol						
10 wt%	–	1.57	1.3	1.3	1.28	1.2
15 wt%	5.5	1.38	1.22	1.2	1.11	1.08
20 wt%	1.24	1.22	1.2	1.17	1.16	1.05
Selectivity (O_2/N_2)-methanol						
10 wt%	1.6	1.37	1.33	1.25	1.18	1.14
15 wt%	5.64	1.75	1.47	1.39	1.18	1.11
20 wt%	3.62	1.6	1.31	1.24	1.19	1.08

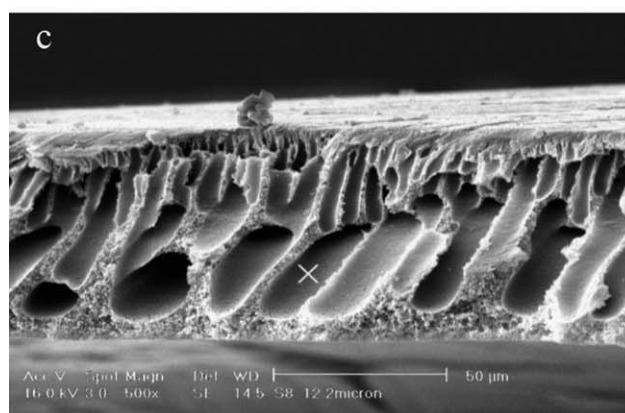
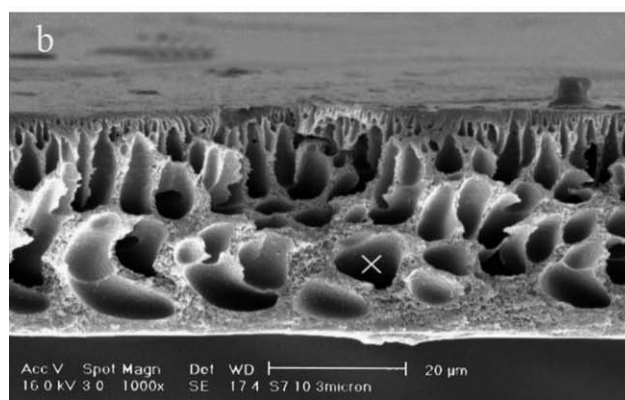
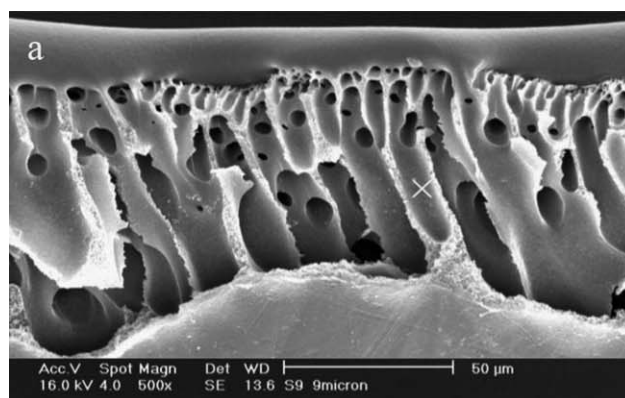


Figure 13 Cross-sectional SEM micrographs of the prepared membrane (20 wt % PES) in NMP as solvent, immersed in ethanol/ H_2O coagulation bath and coated with 3 wt % PDMS (a) 10/90 wt %, (b) 15/85 wt %, (c) 20/80 wt %.

ture). The formation of PES membranes soaked in methanol/ H_2O 20 : 80 wt % was faster as the result of decreasing the solubility parameter of binary nonsolvent mixture and solubility parameter difference between solvent and nonsolvent mixture. Solvent can be attracted with nonsolvent mixture and this caused creation of the wider and longer pores. The spherical pores in sublayer changed to wide finger-like pores, as shown in Figure 13(c).

Permeance and selectivity results are presented in Figure 14 and Table VIII, respectively. The results

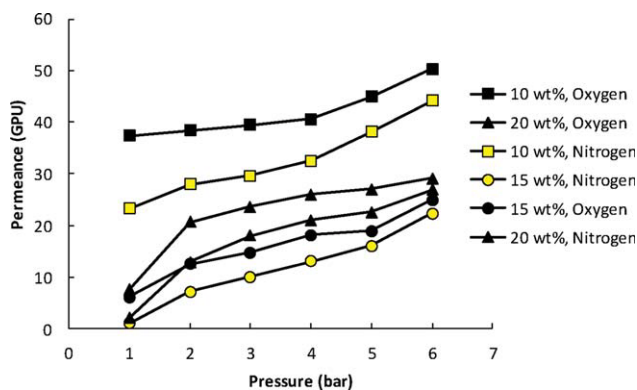


Figure 14 Influence of methanol addition in coagulation bath on permeance of membrane (20 wt % PES) in NMP as solvent coated with 3 wt % PDMS (support layer 75 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

illustrate that the permeance changes have the contrary trend with solubility parameter difference between solvent and nonsolvent mixture; for instance, when this parameter was low, higher permeance was obtained.

CONCLUSIONS

The composite membranes of polyethersulfone coated by polydimethylsiloxane were prepared by wet phase inversion technique in the presence of additives in different conditions. The following results were obtained from this study:

1. Support and coating polymer concentration can control the permeance.
2. Thickness must be adjusted with two viewpoint, satisfied permeance and mechanical strength.
3. Solvent should be selected based on the desired structure, for instance finger-like structure with dense layer is required for air separation.
4. By appropriate adding of PVDF to the PES casting solution, porous membranes with suitable permeance and morphology are formed.
5. Addition of optimized low molecular weight alcohol such as ethanol and methanol in the casting solution and coagulation bath improve the properties of the membrane. Solubility parameters plays important role to control membrane structure.
6. The permeance changes have the direct trend with solubility parameter difference between polymer and solvent mixture, for instance when this parameter difference was low, inadequate permeance was obtained.
7. The permeance changes have the contrary trend with solubility parameter difference

between solvent and nonsolvent mixture, for instance when this parameter difference was low, higher permeance was obtained.

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