Separation of CO_2 from CH_4 by Pure PSF and PSF/PVP Blend Membranes: Effects of Type of Nonsolvent, Solvent, and PVP Concentration

Pourya Moradihamedani, Nor Azowa Ibrahim, Wan Md Zin Wan Yunus,* Nor Azah Yusof

Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
Correspondence to: N.A. Ibrahim (E-mail: norazowa@science.upm.edu.my)
*National Defence University of Malaysia, Kem Sungai Besi, 57000, Kuala Lumpur, Malaysia

ABSTRACT: Complete CO_2/CH_4 gas separation was aimed in this study. Accordingly, asymmetric neat polysulfone (PSF) and PSF/polyvinylpyrrolidone (PVP) blend membranes were prepared by wet/wet phase inversion technique. The effects of two different variables such as type of external nonsolvent and type of solvent on morphology and gas separation ability of neat PSF membranes were examined. Moreover, the influence of PVP concentration on structure, thermal properties, and gas separation properties of PSF/PVP blend membrane were tested. The SEM results presented the variation in membrane morphology in different membrane preparation conditions. Atomic forced microscopic images displayed that surface roughness parameters increased significantly in higher PVP loading and then gas separation properties of membrane improved. Thermal gravimetric analysis confirms higher thermal stability of membrane in higher PVP loading. Differential scanning calorimetric results prove miscibility and compatibility of PSF and PVP in the blend membrane. The permeation results indicate that, the CO_2 permeance through prepared PSF membrane reached the maximum (275 ± 1 GPU) using 1-methyl-2-pyrrolidone as a solvent and butanol (BuOH) as an external nonsolvent. While, a higher CO_2/CH_4 selectivity (5.75 ± 0.1) was obtained using N-N-dimethyl-acetamide (DMAc) as a solvent and propanol (PrOH) as an external nonsolvent. The obtained results show that PSF/PVP blend membrane containing 10 wt % of PVP was able to separate CO_2 from CH_4 completely up to three bar as feed pressure. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

A wide variety of applications are available for gas separation, including especially physical and chemical adsorption.[1,2] Currently, membrane processes are considered as promising technology for gas separation because of its simplicity, i.e. no absorbent, which has to be regenerated, low capital cost, less space requirement, environmental friendliness, and low energy consumption.[3,4] There are several applications for gas separation membranes such as hydrogen separation, oxygen/nitrogen separation, carbon dioxide/methane separation, natural gas separation, vapor/vapor separation, and dehydration of air.[5] Since, CO_2 possesses the most greenhouse effect, CO_2 removal is more attractive among other gas separation processes by polymeric membrane.[1,6] Furthermore, CO_2 removal can be taken into account for natural gas upgrading and enhanced oil recovery.[6]

There are many studies, which show that PSF has been extensively employed to fabricate blend and mixed matrix gas separation membrane for CO_2/CH_4 separation because of its satisfactory gas permeance and acceptable selectivity.[7–9] Moreover,

the role of PVP as an additive in blend membranes for gas separation has been reported recently.[10–16] Since PVP has a good miscibility with PSF, it is used as a suitable organic additive in a primary polymeric solution for fabrication of PSF membranes by phase demixing technique.[17] PSF/PVP blend membrane is less used and novel membrane for gas separation. Ismail and coworkers[10] studied the role of PVP as an additive for gas separation by PSF membrane. According to their result, the gas permeation test results proved that CO_2/CH_4 selectivity of the fabricated membranes improved by the presence of the additives in the following order: PEG < ethanol < PVP < glycerol. Membranes containing PVP are less defective than those containing PEG and ethanol because polymeric property of PVP can increase the combination of polymer chains in the skin layer and as a result a less defective skin layer can be produced. Madaeni and Moradi[11] reported that PVP concentration has an important effect on morphology and performance of asymmetric PSF membrane for gas separation. According to their result, gas selectivity of fabricated membrane improved by increasing PVP concentration in the casting solution. Salleh and Ismail[13] studied the effect

of PVP on the gas separation properties of polyetherimide membrane. According to their result, the thickness of top-layer in membrane containing PVP increased significantly and it causes a membrane with higher CO_2/CH_4 selectivity.

A wide range of investigations has been conducted by researchers to clarify the process of membrane formation during the phase inversion method. Madaeni and Moradi[11] reported two kinds of demixing during membrane formation; instantaneous and delayed phase–phase demixing. Instantaneous demixing produces membranes with highly porous sublayers including macrovoid and large pores and very thin active layer. Whereas, membranes generated by delaying phase separation mechanism show less porous support layer containing closed cell and large pores free substructure with a thick and dense top layer.[10,11,17,18] Currently, this research is aimed to separate CO_2 from CH_4 completely using asymmetric membranes. Three important variables were considered in this task including of type of nonsolvent utilized in the coagulation bath, type of solvent in the casting solution, and PVP concentration in PSF/PVP blend membrane. The morphology, performance, and thermal properties of prepared membranes were examined.

EXPERIMENTAL

Materials

Polysulfone (PSF) resin with the average $M_n = 22,000$ was purchased from Sigma-Aldrich. The organic solvents and nonsolvents include, 1-methyl-2-pyrrolidone (NMP), *N-N*-dimethyl-acetamide (DMAc), ethanol (EtOH), propanol (PrOH), and butanol (BuOH) were purchased from Merck (Germany). Polyvinylpyrrolidone (PVP) with 25,000 g mol^{-1} molecular weight was supplied from Merck (Germany). CO_2 and CH_4 gases were provided in 40 L cylinders with a purity of 99.99%.

Preparation of Pure PSF and PSF/PVP Blend Membranes

In this research, wet–wet phase demixing technique was used for fabrication of neat PSF and PSF/PVP blend membranes. In wet–wet phase separation process, membranes are formed by contacting polymer solution with two nonsolvent baths in series. The first bath is used to obtain a concentrated layer of polymer at the interface. This step makes ultra-thin top layer similar to the evaporation step of dry–wet phase separation process. The second bath is responsible for the actual coagulation to be precipitated. The choice of nonsolvents for the bath strongly depends upon the type of solvent to be dissolved in the polymer solution. The important variables for preparation of pure PSF and PSF/PVP blend membranes were summarized in Table I. The components of casting solution for pure PSF membrane were PSF resin with the 22 and 78 wt % of the solvent. NMP and DMAc were used as solvents separately. While, for PSF/PVP blend membrane the casting solution was included of PSF (22 wt %), PVP (5 and 10 wt %) and NMP as solvent. After preparing the homogeneous solution, this solution was kept at room temperature for 24 h for removal of air bubbles and then cast on a smooth glass plate by film casting knife with a thickness of 350 μm. The wet film was then immersed in the first coagulation bath using various nonsolvents such as; EtOH 20%, PrOH 20%, and BuOH 20% for 90 s. After liquid–liquid phase demixing in the first nonsolvent bath, prepared membrane was transferred to second coagulation bath of distillate

Table I. Variables and Conditions Considered for Preparation of Membranes

Membrane (20%)	Solvent	Additive	Nonsolvent (20%)
PSF 22%	NMP 78%	–	EtOH
PSF 22%	NMP 78%	–	BuOH
PSF 22%	NMP 78%	–	PrOH
PSF 22%	DMAc 78%	–	PrOH
PSF 22%	NMP 73%	PVP 5 wt %	PrOH
PSF 22%	NMP 68%	PVP 10 wt %	PrOH

water and soaked for 24 h. This is to ensure all of the solvents in the structure of the membrane are replaced by nonsolvents. Lastly, PSF membranes were dried at the room temperature for 1 day.

Scanning Electron Microscopy (SEM)

The morphology of developed membranes was characterized by SEM (Philips XL-30). To evaluate the cross-section view of the membranes, our samples were fracture cryogenically within liquid nitrogen. The samples were then spattered with gold and viewed at 5.0 kV.

Atomic Forced Microscopy (AFM)

The morphology of membrane surface, in terms of the mean surface roughness (Ra), was analyzed by atomic force microscopy (Ambios Q-scope) in tapping mode. Samples with size of 5×5 μm^2 surface area were scanned at 0.8 Hz. Roughness parameters were determined through the AFM analysis software (Nano scope Software Version). There exists mean roughness (Ra), root mean square of Z data (Rq), and mean difference in the height between the five highest peaks and the five lowest valleys (Rz). Ra is the mean value of surface area relative to the center plane, for which the volume enclosed by the image above and below this plane is equal. Rq is the standard deviation of Z-values within the given area.[19,20]

FTIR Spectroscopy

To better understand of the PSF and PVP interaction in the prepared blend membranes, fourier transform-infrared spectroscopy (Series100 PerkinElmer FT-IR 1650) was carried out in the wave number range of 300–1800 cm^{-1}. Since, each specific functional group has a characteristic strength area, four samples with different PVP loadings were examined by FTIR spectroscopy.

Differential Scanning Calorimetry (DSC)

To identify the glass transition temperature (T_g) of pure PSF and PSF/PVP blend membranes, DSC characterization was utilized with Mettler Toledo DSC822e thermal analysis instrument with a heating rate of 10°C min^{-1} from 80°C up to 240°C. DSC results can be used to determine the miscibility and compatibility of PSF and PVP in the blend membrane.

Thermal Gravimetric Analysis (TGA)

To examine the variation in physical properties of fabricated membranes before and after cross-linking, thermal gravimetric
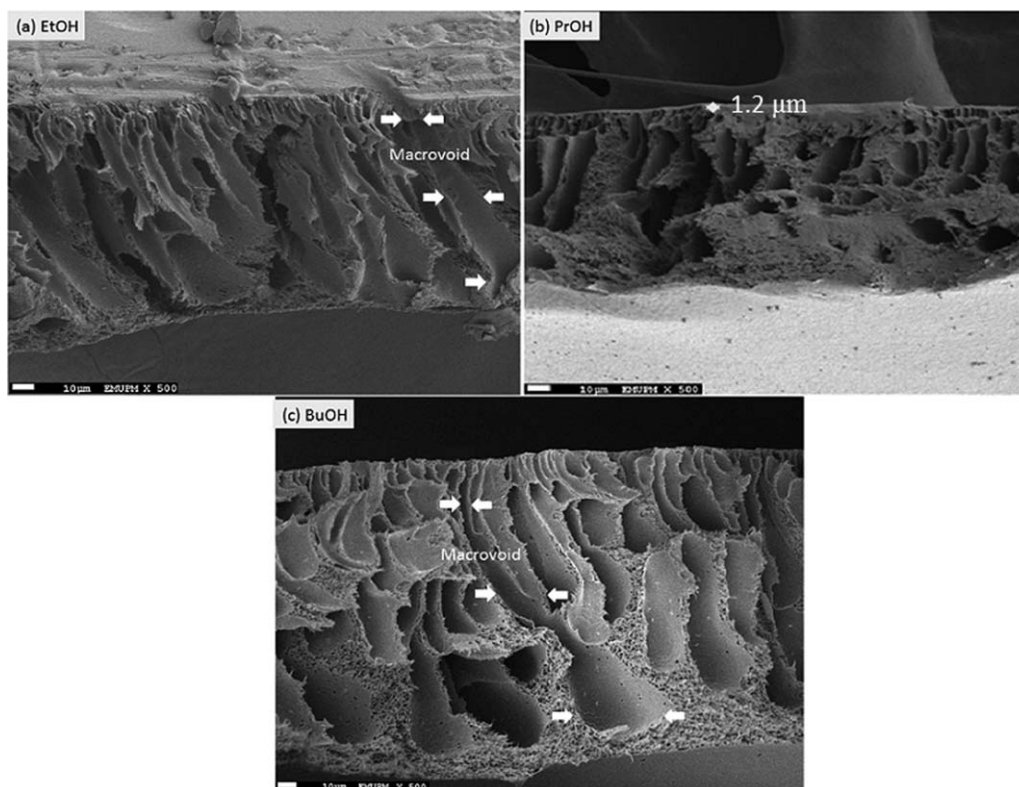
Figure 1. SEM photographs of cross-sections of neat PSF membranes using different nonsolvents (a) EtOH, (b) PrOH, and (c) BuOH.

analysis with the Perkin Elmar TGA7 instrument was conducted. The TGA characterization was carried out with a heating rate of $10°C$ min^{-1} from room temperature up to $900°C$.

Gas Permeation Evaluation

Gas permeation test of produced membranes for pure CO_2 and CH_4 gases was carried out in the range of 1–3 bar feed pressure. Gas permeation mechanism in polymeric membrane is solution-diffusion. Gases with larger molecular diameter diffuse slower through structure of prepared membrane therefore membrane act as molecular sieve.[21–23] Accordingly, since CH_4 molecular diameter is larger than CO_2,[23] prepared pure PSF and PSF/PVP blend membranes are able to separate these two gases by different selectivities. To evaluate the capability of membranes in gas separation, a filter holder with effective area of 13.8 cm^2 (Merck) was used. In addition, a glass soap bubble flow meter was employed for measuring CO_2 and CH_4 gas flow rates. To ensure accuracy in our experiments, the gas permeation test was repeated twice in the steady state. The gas permeance (P L^{-1}) was calculated using the eq. (1)

$$PL^{-1} = QA^{-1}\Delta P^{-1} \qquad (1)$$

where P is permeability, L is membrane top layer thickness, Q is gas flow (at standard pressure and temperature), A is the effective membrane area in cm^2, and ΔP is the differential partial pressure across the membrane. The usual unit of permeance is GPU and 1GPU is equal to 1×10^{-6} $cm^3(STP)$ cm^{-2} s^{-1} $cmHg^{-1}$. Equation (2) can be used to calculate CO_2/CH_4

selectivity. Where P_i and P_j are CO_2 and CH_4 permeance, respectively.

$$a = P_i P_j^{-1} \qquad (2)$$

RESULTS AND DISCUSSION

Effects of Type of External Nonsolvent on Membrane Morphology and Performance

Type of solvents and nonsolvents used in the preparation step, plays a crucial role in controlling membrane structure and performance.[24] PSF membranes can be prepared using NMP and various nonsolvents.[25–27] Figure 1 indicates the cross-section view of PSF membranes produced by NMP as solvent and various external nonsolvents. All of nonsolvents used have different influence on the prepared membrane in term of porosity, top layer, and macrovoids structure. As shown in Figure 1(a,c), very porous structure containing macrovoids, which began from the surface layer and continued up to the support layer is clear for membranes prepared by EtOH and BuOH as nonsolvents. While by using PrOH as a nonsolvent, a membrane containing less porous support layer and macrovoid free structure was obtained [Figure 1(b)].

This phenomenon obviously affected the membrane performance (Figure 2). As shown in Figure 2, the CO_2 permeance is the lowest in the various feed pressures for PrOH as a nonsolvent. Whereas, this number increased for EtOH and reached to a maximum for BuOH. Type of nonsolvents also affects
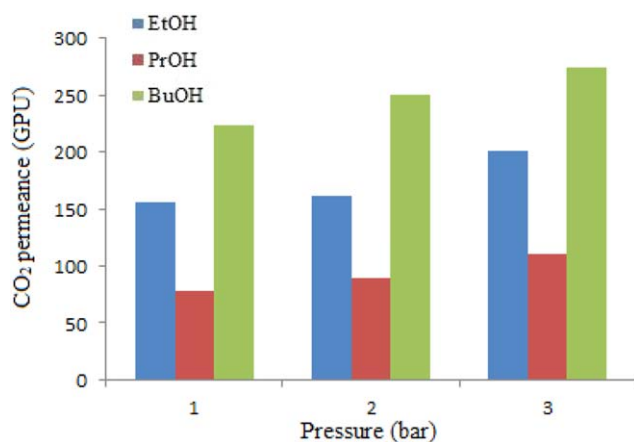
Figure 2. CO_2 permeance of pure PSF membranes using different nonsolvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

membrane selectivity with respect to CO_2 and CH_4 gases. As revealed in Table II, membrane fabricated from BuOH as a nonsolvent has a minimum value of selectivity. While, this number is the highest for membrane produced by PrOH in the coagulation bath. The reason for obtaining various morphologies and performances of asymmetric PSF membranes is different liquid–liquid phase demixing between solvent and nonsolvent in the coagulation bath. Fast demixing of solvent and nonsolvent, causes membranes with highly porous structure whereas, delayed demixing produces membrane with macrovoids free structure and thick surface layer.[22,28] To identify the type of phase demixing in the membrane preparation process, solubility parameters differences between nonsolvent and solvent were shown in Table III. The calculation method of solubility parameters for nonsolvents containing different components (alcohol and water) was explained in previous research.[11]

According to the nonsolvents used, the difference between solubility parameters of NMP and nonsolvents are in the following order: BuOH > EtOH > PrOH. Lower difference between the solvent and nonsolvent solubility parameter (NMP-PrOH) causes delayed liquid–liquid phase demixing and consequently produces membrane with lower porous structure and thicker top layer [Figure 1(b)]. On the contrary, the higher difference between solvent and nonsolvent solubility parameter, produces membrane with the higher porous structure and the thin surface layer [Figure 1(a,c)].[22,28] There are many studies, which prove that even the small amount of difference between solvent and nonsolvent solubility parameters among various solvent/

Table II. CO_2/CH_4 Selectivity of Neat PSF Membranes Using Different External Nonsolvents

Nonsolvents/ Pressures	CO_2/CH_4 selectivity (± 0.1)		
	1 bar	2 bar	3 bar
EtOH 20%	2.2	1.7	1.3
PrOH 20%	3.7	2.5	1.8
BuOH 20%	1.8	1.3	1.1

Table III. Solubility Parameter Differences Between Nonsolvents and Solvents

Nonsolvents and solvent	Solubility parameters $(MJ\ cm^{-3})^{1/2}$	Solubility parameter differences with NMP $\Delta\delta_{(N-S)}$
EtOH 20%	43.52	20.62
PrOH 20%	43.18	20.28
BuOH 20%	44.06	21.16
NMP (Solvent)	22.9	–

nonsolvent pairs causes a distinct influence on morphology and performance of prepared membranes.[22,26,29] For example, Iqbal et al.[29] studied the effect of different nonsolvents used in coagulation bath on morphology and performance of PC membrane using DMAc as solvent. According to their result, solubility parameter differences between DMAc with EtOH, PrOH, and BuOH are 16.24, 16.56, and 16.75, respectively. Although there are small solubility parameter differences among various DMAc/nonsolvents pairs, fabricated membranes have noticeable differences in morphology and gas separation properties.

Effects of Type of Solvent on Membrane Morphology and Performance

To improve membrane selectivity, two different types of solvent (NMP and DMAc) were used separately. By employing NMP as a solvent for preparation of casting solution, the best obtained selectivity was 3.7 using PrOH as coagulation bath at 1 bar feed pressure (Table II). Since, the membrane selectivity is a crucial option for assessment of membrane performance; this study aims to achieve the efficient separation of CO_2 from CH_4. In an attempt to fulfill this purpose, the solvent changed from NMP to DMAc using PrOH as nonsolvent in the coagulation bath. Figure 3 shows the SEM photograph of cross-section view of membrane fabricated by DMAc as solvent. The membrane produced by DMAc has a thick top layer and macrovoids free
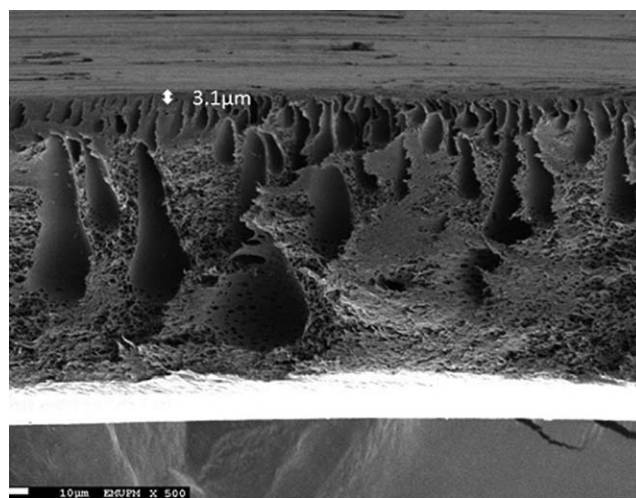

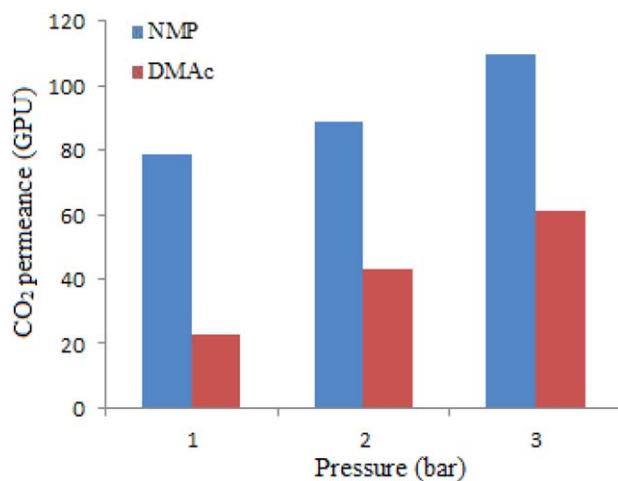**Figure 3.** SEM photograph of cross-section of neat PSF membrane using DMAc as solvent.

Figure 4. CO_2 permeance of PSF membranes using different solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure (Figure 3) in comparison with the membrane prepared by casting solution containing NMP as a solvent [Figure 1(b)].

These differences in the membrane morphology affected the performance of membranes in terms of gas permeance and selectivity. As shown in Figure 4, CO_2 permanence of produced membrane declined significantly from NMP to DMAc in different feed pressures while a noticeable increase in gas selectivity is detectable by using DMAc instead of NMP in the casting solution (Table IV).

Variations in the membrane morphology as well as gas permeance and gas selectivity are reflected by differences in solubility parameters of polymer and solvents, which lead to the different rate of demixing between polymer and solvent in the casting solution. Instantaneous phase demixing creates membrane with highly porous structure whereas delayed demixing produces membrane with less porous support layer and thick active layer.[29,30] Solubility parameter differences between solvents and polymer can be observed in Table V. As indicated in this table, solubility parameter differences of NMP-PSF is more than DMAc-PSF. Accordingly, DMAc has a higher interaction with PSF in comparison with NMP. Then PrOH, which being employed in coagulation bath is not able to diffuse easily into the polymeric film. This phenomenon causes delayed demixing, which is accompanied with a less porous support layer and a thick surface layer.[29,30]

PSF/PVP Blend Membranes with Different Concentration of PVP

Since this study is aimed to separate CO_2 from CH_4 completely, PSF/PVP blend membranes were prepared. Variation in thermal

Table IV. CO_2/CH_4 Selectivity of Neat PSF Membranes Using Different Solvents

Solvents/Pressures	CO_2/CH_4 selectivity (± 0.1)		
	1 bar	2 bar	3 bar
NMP	3.70	2.50	1.80
DMAc	5.75	3.90	1.80

Table V. Solubility Parameter Differences Between Solvents and Polymer[31]

Solvents and polymer	Solubility parameters (MJ cm^{-3})$^{1/2}$	Solubility parameter differences with PSF $\Delta\delta_{(S-P)}$
NMP	22.90	2.64
DMAc	22.70	2.44
PSF	20.26	–

properties, morphology, and performance of PSF/PVP blend membranes including different amounts of PVP (5 and 10 wt %) has been reported in this article. To examine the miscibility and compatibility of PSF and PVP, the glass transmission temperature (T_g) of pure PSF as well as PSF/PVP blend membrane was measured using DSC. Employing DSC characterization for study of the compatibility of polymer blends has been extensively employed in previous researches.[32,33] As depicted in Figure 5, T_g value is around 180°C for pure PSF membrane. However, this number increased clearly and reached about 190°C by addition of PVP to casting solution. Single T_g value for PSF/PVP blend membrane, proves the miscibility between these two polymers. Similar results were obtained by Ismail and Rafizah.[33] To survey the interaction of PSF and PVP in PSF/PVP 5 and 10 wt % blend membranes at the molecular level, FTIR spectroscopy was utilized. There were several researches, which FTIR spectroscopy employed to study the interactions at the molecular level of blend polymers.[34–36] In FTIR spectroscopy, the spectra of incompatible blend polymers are the sum of the spectra of pure polymers. Whereas, interactions between functional groups of polymers in miscible blends is detected by frequency shifts or transmittance intensity variations.[37] As indicated in Figure 6 the comparison between spectra of pure PSF membrane and PSF/PVP blend membrane, shows the interaction between functional groups of PSF and PVP through variation in frequency shifts as well as transmittance intensity. The peaks in the range of 1657–1663 cm^{-1} was detected for the
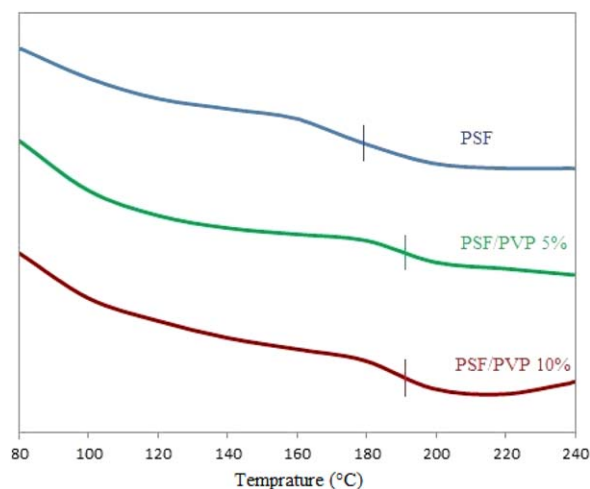

Figure 5. DSC curves of pure PSF, PSF/PVP 5 wt % and PSF/PVP 10 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
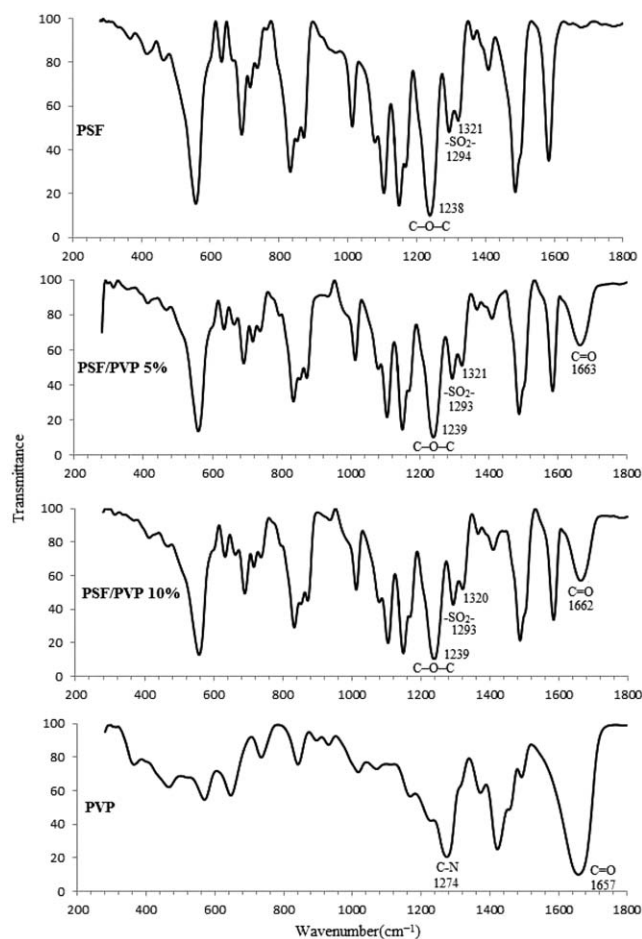
Figure 6. FTIR spectra of pure PSF, pure PVP, PSF/PVP 5 wt%, and PSF/PVP 10 wt %.
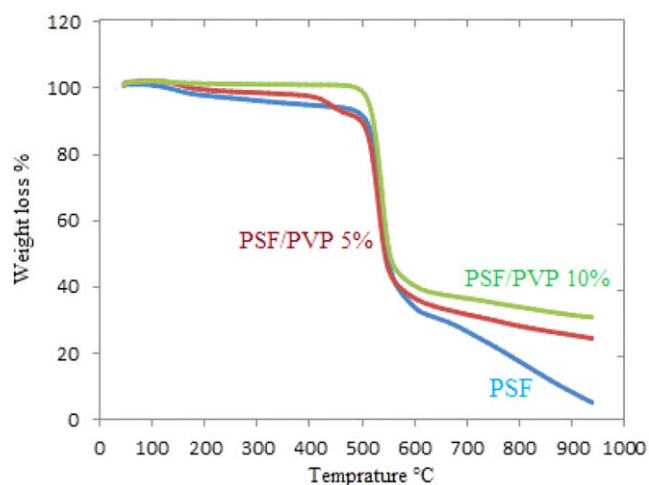

Figure 7. Thermogarvimetric analysis of membranes with different PVP loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cm^{-1}) and C—O—C groups (1238–1239 cm^{-1}) in PSF, respectively. Additionally, the peak which placed around 1273 cm^{-1} in pure PVP spectra is not visible in spectra of blend PSF/PVP membranes. Possibly the frequency of the mentioned peak changed or its transmittance intensity improved and overlapped with the SO$_2$ functional group (1293 cm^{-1}) in PSF.

Since thermal stability plays an important role in gas separation at high temperatures, there are many studies, which thermal stability of prepared blend membranes examined by TGA characterization.[21,26] TGA results of prepared membranes are illustrated in Figure 7. Since, solvents in the wet film are replaced by nonsolvents in coagulation bath, weights of specimens were approximately constant in temperatures around 25–170°C, indicating whole solvent removal. As shown in Figure 7, there is a crucial weight loss in temperature range of 500–550°C, which attributed to polymer decomposition.

Figure 8 shows cross-section view of asymmetric membranes with different PVP loading (5 and 10 wt %). As shown in Figure 8(a), when concentration of PVP in casting solution is 5 wt %, a membrane containing very long macrovoids and finger-like pores in structure without remarkable surface layer was
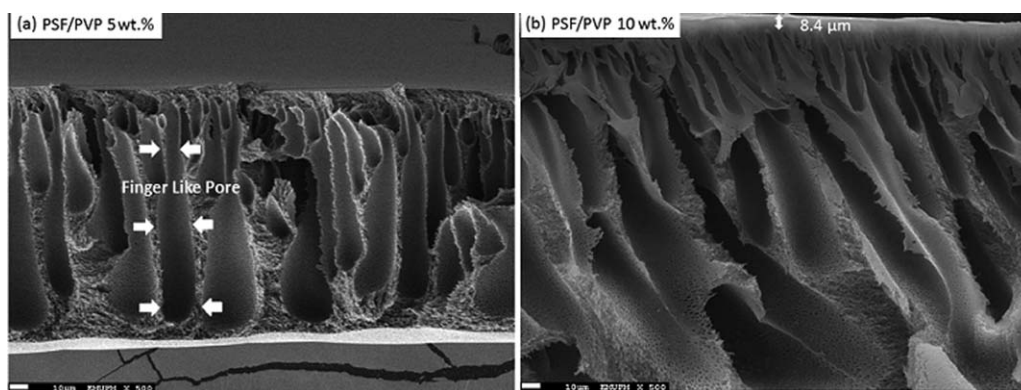
C=O functional group in PVP. This peak discloses the existence of PVP in PSF/PVP blend membranes. Furthermore, the intensity of this peak increased in higher PVP concentration. The most significant shift, which is around 6 cm^{-1} (1663–1657 cm^{-1}) is related to C=O bond in PVP. The second important shifts which is about 1–2 cm^{-1} is linked to the sulfonate stretching mode (—SO$_2$—) (1321–1320 cm^{-1} and 1294–1293

Figure 8. SEM photographs of cross-sections of the membranes with different PVP loadings (a) PSF/PVP 5 wt % and (b) PSF/PVP 10 wt %.
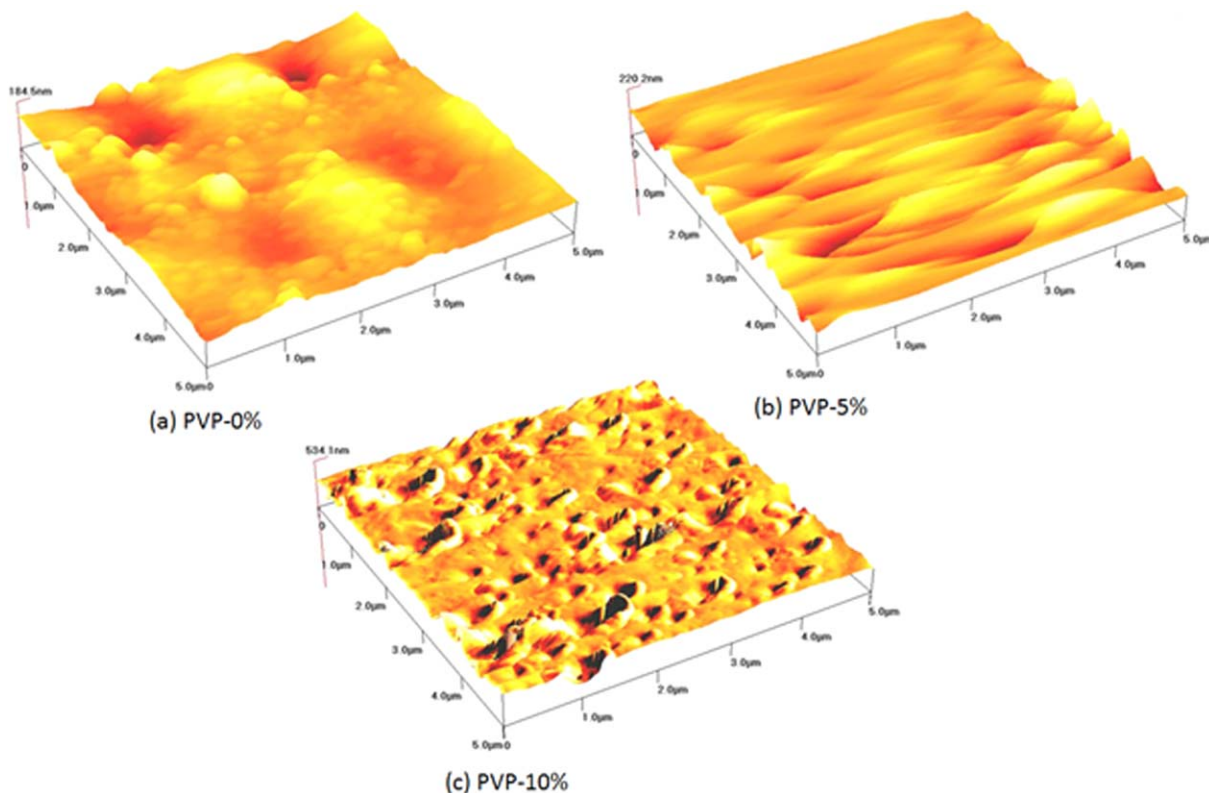
     WILEY ONLINE LIBRARY

Figure 9. The three-dimensional AFM surface images of the membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

produced. Whereas, in a neat PSF membrane [Figure 1(b)] the length of pores is lower and thickness of surface layer is also higher. In a higher PVP concentration (10 wt %), thickness of the active layer in prepared membrane increased significantly and lower porosity is observable in support layer [Figure 8(b)]. Figure 9 presented three-dimensional AFM images of membranes surface layer. Within the scan area 5×5 μm^2, obviously the Ra, Rq, and Rz were first reduced when PVP content increased from 0% to 5%. Then, they improved when PVP content increased from 5% to 10% (shown in Table VI). Since, the roughness parameters depend on the Z-value, which is the vertical distance that the piezoelectric scanner moves, this relationship is anticipated. When the surface includes deep depressions and high peaks, the tip moves up and down over a wide range and the roughness parameter of the surface is high. The roughness parameters of membranes decreased when 5 wt % of PVP were introduced. This fact could be explained through membrane

Table VI. Surface Roughness Parameters of PSF/PVP Membranes

Scanning area 5×5 μm^2	Roughness (nm)		
	Ra	Rq	Rz
PVP-0 114.30	13.63	18.47	114.30
PVP-5% 117.50	11.80	18.29	117.50
PVP-10% 312.80	29.99	47.40	312.80

without any detectable surface layer [Figure 8(a)]. While, a distinct increase in roughness parameters was observed by addition of 10 wt % of PVP to the casting solution, which could be justified by thick surface layer of prepared membrane as a result of high PVP loading [Figure 8(b)]. In fact, higher surface roughness led to better separation properties of fabricated membrane.[38] Variations in the membrane morphology with different PVP loadings, affected membrane performance in the terms of gas permeance, and selectivity.[11] CO_2/CH_4 separation properties of fabricated membranes with different PVP concentrations are depicted in Figure 10. By addition of 5 wt % of PVP in casting solution, CO_2 and CH_4 permeability increased significantly in comparison with neat PSF membrane [Figure 10(a,b)]. While, by increasing PVP concentration up to 10 wt %, a membrane with the best performance in term of CO_2/CH_4 separation was produced. As illustrated in Figure 10(c), membrane containing 10 wt % of PVP, is able to separate CO_2 from CH_4 completely. Furthermore, variation in CO_2/CH_4 selectivity in different PVP loadings has been shown in Table VII. As mentioned in this table, CO_2/CH_4 selectivity of membrane reached to a minimum by addition of 5 wt % of PVP. Whereas, a full CO_2/CH_4 selective membrane was produced by addition of 10 wt % of PVP. These variations in membrane morphology and performance in different PVP loadings is justified by interactions between components in casting solution as well as different phase demixing kinetics.[30] The function of PVP in 5 wt % in casting solution is a pore former, which leading to a membrane with highly porous support layer
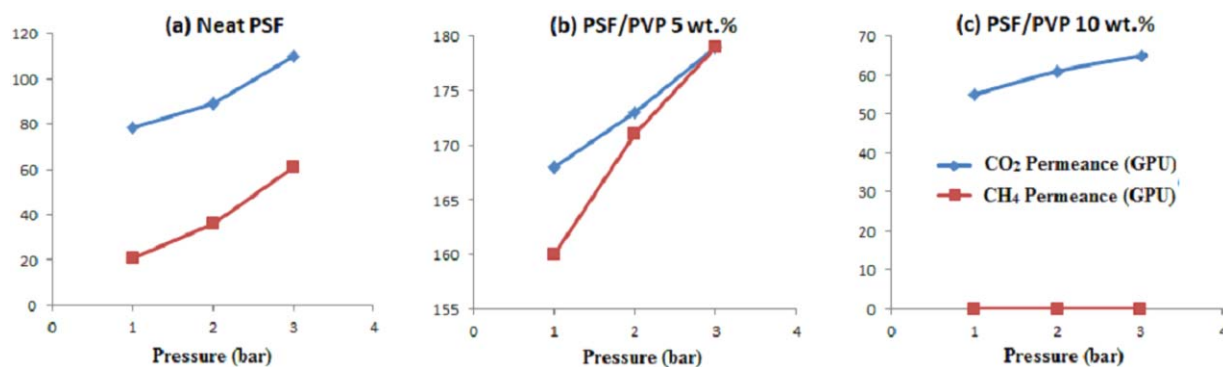
Figure 10. Gas permeance in different PVP loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with a very thin active layer. While, in 10 wt % of PVP in casting solution, interaction of PVP with NMP as solvent improved and causes delayed liquid–liquid phase demixng. Hence, a membrane with a distinctive surface layer and less porous support layer was produced. In another word, high concentration of PVP can improve the coalescence of polymer chains in the surface layer and then a less defective top layer can be obtained. Gas permeation mechanism through prepared PSF/PVP membranes is solution diffusion and membranes act as a molecule sieve.[21–23] Consequently, since PSF/PVP 10 wt % has very thick top-layer [Figure 8(b)], it is possible that size of pores diameter at the structure of fabricated membrane are smaller than CH_4 molecular diameter (larger molecule in comparison with CO_2[23]) then just CO_2 molecules are able to pass through membrane [Figure 10(c)].

CONCLUSIONS

To separate CO_2 from CH_4 completely, flat sheet asymmetric pure PSF, and PSF/PVP blend membranes were fabricated. The effects of three different types of external nonsolvent and two different types of solvent on morphology and performance of pure PSF membrane were examined and it was found that pure PSF membrane, which was prepared by DMAc as solvent in casting solution and PrOH as external nonsolvent in coagulation bath has a higher gas selectivity in comparison with PSF membrane prepared by NMP as solvent in casting solution and EtOH or BuOH as coagulators.

Since, the purpose of this study was to separate CO_2 from CH_4 completely, PSF/PVP blend membranes were prepared. Morphology, thermal properties, and performance of PSF/PVP

Table VII. CO_2/CH_4 Selectivity of PSF/PVP Blend Membranes Containing Different PVP Loadings

Membrane/Pressures	CO_2/CH_4 Selectivity (±0.1)		
	1 bar	2 bar	3 bar
Neat PSF	3.70	2.50	1.80
PSF/PVP 5 wt %	1.05	1.01	1.00
PSF/PVP 10 wt %	∞	∞	∞

blend membranes containing different concentrations of PVP were investigated. According to SEM photographs, high concentration of PVP causes membrane with thicker top layer. Also, AFM results demonstrated the higher PVP loading, the higher surface roughness parameters. As a result of these phenomena and also gas permeation mechanism of prepared membrane (solution diffusion and molecule sieve), blend membrane containing 10 wt % of PVP was able to separate CO_2 from CH_4 completely up to three bar as feed pressure.

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