

Fabrication and Evaluation of a Blend Facilitated Transport Membrane for CO₂/CH₄ Separation

Liyuan Deng* and May-Britt Hägg*

Department of Chemical Engineering, Faculty of Natural Sciences and Technology, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

ABSTRACT: This Article focuses on the optimization of the fabrication procedure and preparation conditions of a polyvinylamine/poly(vinyl alcohol) (PVAm/PVA) blend membrane with respect to its CO₂/CH₄ separation performance at elevated pressures and the up-scaling of the PVAm/PVA blend flat sheet membrane for pilot scale tests. Experiments show that the optimized membrane preparation conditions for CO₂/CH₄ separation are different from those for CO₂/N₂ separation, especially when operating at elevated pressures, which is considered for applications such as biogas upgrading. The effects of membrane preparation conditions were investigated and membrane CO₂/CH₄ separation performance was evaluated at elevated pressures (CO₂ partial pressure up to 5.6 bar). Up-scaled flat sheet membranes (300 × 300 mm) were prepared using a dip-coating procedure. The selection of the support substrate and aging of the membrane were also investigated. A CO₂ permeance of up to 0.58 m³ / (m² h bar), and a CO₂/CH₄ selectivity of up to 45 were documented at 2 bar with 10% CO₂ in feed gas. The membrane showed excellent stability over a 5-month test.

1. INTRODUCTION

The decisive requirements for an industrial CO₂-selective membrane are high CO₂ selectivity and a high CO₂ permeation rate to increase the product purity, reduce the product loss and lessen the required membrane area.^{1–7} From a practical point of view, the membrane must also have good mechanical properties and durability in operating conditions with a long lifetime, and be easy to fabricate at a low cost. The development of membrane materials with the desired intrinsic properties is believed to be the key. Recently, some new CO₂-selective membrane materials have been reported,^{8–25} and the fixed-site-carrier (FSC) membranes have become highlighted due to their excellent CO₂ separation performance resulting from the unique CO₂ facilitated transport mechanism.^{26–40} In fixed-site-carrier (FSC) polymeric membranes, the functional groups are bound chemically (covalently) or physically to a solid polymer matrix as the CO₂ facilitated transport carriers, exhibiting high CO₂ permeance and selectivity, as well as good stability.^{30–34,39} Polyvinylamine (PVAm) has been reported as one of the best FSC membrane materials,^{27,30} which has the highest content of carriers (over 30% amino groups) among all amine-containing polymers. In this membrane, CO₂ transports through the water-swollen FSC membrane in the form of HCO₃[−] and thus diffuses as ions in liquids. The membrane combines the excellent separation performance of supported liquid membranes with good stability and processability of solid polymeric membranes.²⁷

A PVAm composite membrane with an in-house synthesized PVAm (MW 80 000) selective layer on a polysulfone (PSf) ultrafiltration support was reported by Hägg et al.^{30,41} Recently a PVAm membrane prepared from a commercially available PVAm of high molecular weight (MW 340 000) was reported for CO₂/N₂ separation.^{42,43} The membrane exhibited facilitated transport characteristics with a very high selectivity of CO₂ over N₂ and CH₄. A PVAm of lower molecular weight is believed to have a higher CO₂ permeance since chains in polymers with a

lower molecular weight are usually more flexible, while the diffusivity of gases through dense polymer membranes are dependent on the mobility of the polymer chains.^{1,4} However, a dry film of low molecular weight PVAm (e.g., MW 25 000) is usually brittle, and the water-swollen PVAm film is weak and sticky, resembling a fluid of high viscosity. These drawbacks made it very difficult to fabricate PVAm as an ultrathin selective layer on a porous support. In addition, the pore-filling phenomenon (polymer solution filling in the pores of the support) occurred during coating, which adds additional resistance to the gas permeation and causes serious loss of gas flux because of the blocked micropores in the support. In our previous work, the blending of PVAm with a mechanically robust polymer, poly(vinyl alcohol) (PVA) was used to provide mechanical integrity to the membrane. A PVAm/PVA blend membrane was developed and a comprehensive study on the facilitated transport mechanism of this membrane was reported with the main focus on its CO₂/N₂ separation performance,²⁷ where PVAm and PVA were proven compatible and the PVAm/PVA blend was homogeneous: only one melting point (*T*_m) was observed in the DSC graph, which is different from those of PVAm and PVA.

This membrane has been found suitable for CO₂ separation from other CO₂ sources as well, such as CO₂/CH₄ separation. The homogeneous blending of PVAm and PVA enables the membrane to take advantages of the properties of both polymers, bringing in high CO₂ permeance and selectivity (PVAm), as well as good mechanical strength and stability (PVA), which is considered beneficial for separation at elevated pressures, such as in biogas upgrading applications. As these

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applications are for different gas systems other than the previously studied CO₂/N₂ system, and the operating pressures are relatively higher, the membrane preparation procedure and optimized conditions must also be adjusted to make a membrane with desired performance for these applications.⁴⁴

The purpose of the current Article is to report the further optimization of the PVAm/PVA blend membranes with the focus on the optimization of fabrication procedure and the evaluation of separation of CO₂/CH₄, especially for its applications at elevated pressure for biogas upgrading. One way to handle high pressures (e.g., >20 bar) is to introduce nanofillers into membrane matrix, such as using carbon nanotubes.⁴⁴ For applications at low or elevated pressures (~20 bar), however, it is not necessary to use nanofillers, as the fabrication then becomes more complicated and the cost significantly increases. Moreover, the PVAm/PVA blend membrane has strong mechanical strength to resist the compact effect at elevated pressures (e.g., up to 20 bar). The detailed description on the preparation procedures and optimization of parameters of the fabrication of the ultrathin, defect-free PVAm/PVA blend FSC membranes may provide valuable technical information on this category of membranes. However, this part of the work has never been published.

In the current Article, the preparation parameters and procedures were optimized accordingly to improve the CO₂/CH₄ separation performance for applications at elevated pressures. The separation performances of the membrane at different preparation conditions were tested, and the effects of the preparation conditions on the CO₂ separation performance were investigated. A specially designed dip-coating vessel for the preparation of membrane with an up-scaled size (300 × 300 mm) is used. An optimized membrane preparation procedure was developed for the up-scaling of the membrane. The membrane morphology was also characterized and the membrane aging and stability were evaluated. Experiments show that the membrane preparation parameters, such as the PVAm content of the PVAm/PVA blend, the heat-treatment method, and the support substrate conditions, exhibit a significant influence on the CO₂ permeance and CO₂/CH₄ selectivity. The morphology of the PVAm/PVA blend composite membrane, including the selective layer thickness and support membrane structure, is an important factor as well. The membrane is very stable over time. A CO₂ permeance of the membrane of 0.58 m³/(m² h bar), and a CO₂/CH₄ selectivity of 45 have been documented at 2 bar with 10% CO₂ in feed gas. According to the process simulation by Deng et al.,⁴⁵ for an on-farm scale biogas upgrading process (0.85-MMscfd raw biogas) using a 2-stage FSC membrane with recycle, it is very profitable if a membrane with CO₂/CH₄ selectivity of 40 and a CO₂ permeance of 0.55 m³(STP)/m²·h·bar at 2 bar, whereas CO₂/CH₄ selectivity of 30 and a CO₂ permeance of 0.2 m³(STP)/m²·h·bar at 10 bar is used.

2. EXPERIMENTAL SECTION

2.1. Materials. Polyvinylamine hydrochloride (PVAm HCl, MW 25 000) was purchased from Polysciences Inc. and 90+% hydrolyzed poly(vinyl alcohol) powder (PVA, MW 72,000) was obtained from Merck Schuchardt. Both were used as received. Sodium hydroxide (NaOH) salt of analytic purity came from Sigma-Aldrich. Polysulfone (PSf) ultrafiltration flat sheet membranes (thickness about 80 μm excluding nonwoven fabric support) of different molecular weight cutoff values (MWCO 20 000 and MWCO 50 000) were purchased from

Alfa Laval, Denmark and used with pretreatment. All pure gases and gas mixtures with certified compositions were supplied in 50 L cylinders (max. 200 bar) by AGA AS, Norway.

2.2. Membrane preparation. PVAm/PVA blend membranes (80 × 80 mm) with a composite structure were prepared by casting the aqueous polymer solution onto the asymmetric PSf ultrafiltration membranes to form ultrathin selective layers of homogeneous PVAm/PVA blends. The polymer solution of PVAm/PVA blend was prepared by adding PVA aqueous solution to a PVAm aqueous solution of the same concentration, 1–5%, depending on the required coating layer thickness and the coating procedure employed. The composition was determined by adjusting the weight ratio of the above solutions. After stirring the mixture overnight and ultrasonic mixing for 2–10 min, the polymer solution was then cast onto a PSf substrate with a calculated amount of blend solution to give the desired thickness by solution casting. The porous substrate was mounted onto a plate using a water proof tape, and a frame was fixed on the top side of the membrane to keep the casting solution staying inside the desired area. The plate was carefully leveled in order to keep the solution even during solvent evaporation. When casting larger sized membranes (300 × 300 mm), dip-coating was used, and in this case the porous substrate was mounted onto a plate using water proof tape and sealed to ensure no solution leaking into the back side of the substrate. Details on the dip-coating procedure in this study can be found in section 3. The PSf support membrane was rinsed with dilute NaOH solution and flushed with distilled water to remove any possible contaminants from the supplier before use. The cast membrane was dried in an oven at 45 °C overnight and cross-linked at 105 °C for 1 h thereafter. Generally two identical membranes were prepared and the tests were repeated to confirm the investigated effects.

The thickness of the dry membranes was confirmed from scanning electron microscopy (SEM) cross-section images. The membranes to be measured after the 15 bar test were gradually depressurized from high pressure to the atmospheric pressure in a humidified environment to recover the membrane to its initial state. The thickness of the membrane to be mentioned hereafter refers to the thickness of the PVAm/PVA blend polymer layer.

2.3. Gas Permeation Measurements. Gas permeation data of a membrane material are the key data that are always checked before and after other parameters are changed (material composition, thickness of selective layer, process conditions and gas composition). Only then can a true picture of the separation properties be obtained and analyzed.

The separation performance of the membranes was tested in a gas permeation setup with a flat sheet type membrane module mounted in a thermostatic cabinet. Another similar setup was used to validate the results on a regular basis. Each of the tests was repeated at least three times. The relative humidity of the system can be adjusted. Except for the experiments to investigate the effect of relative humidity, all the other tests were performed using water saturated feed gas. All membranes were conditioned in the water saturated feed gas for overnight prior to the tests. Details about this setup can be found in.²⁷ Membranes with an effective membrane area of 20 cm² were tested with CO₂/CH₄ gas mixtures (10 vol % of CO₂ and 35 vol % of CO₂) and with the single gases CO₂, CH₄ and N₂ in this study. Operation parameters, such as feed gas flow rate and pressure, temperature, relative humidity, were controlled or recorded directly by Labview software (National Instruments).

Table 1. Permeance Unit Conversion Table

	GPU	m ³ (STP)/m ² ·bar·h	mol/m ² ·Pa·s	m ³ (STP)/m ² ·Pa·s
GPU	1	0.00274	3.38 × 10 ⁻¹⁰	7.60 × 10 ⁻¹²
m ³ (STP)/m ² ·bar·h	365.5	1	1.24 × 10 ⁻⁷	2.78 × 10 ⁻⁹
mol/m ² ·Pa·s	2.96 × 10 ⁹	8.09 × 10 ⁶	1	0.0225
m ³ (STP)/m ² ·Pa·s	1.32 × 10 ¹¹	3.60 × 10 ⁸	44.5	1

A sweep gas was used on the permeate side at atmospheric pressure. The reported relative humidity was recorded right after the membrane cell in the retentate flow. All data documented in this paper was recorded when the system had been stabilized. The permeance of CO₂ (P_{CO_2}) was in the units of m³ (STP)/(m² bar h) and was calculated with eq 1. The selectivity reported in this work is ideal selectivity. The ideal selectivity of CO₂ toward another gas (α) was calculated from the ratio of the permeance of CO₂ and another gas, as expressed in eq 2.^{46,47}

$$P_{\text{CO}_2} = \frac{J_{\text{CO}_2}}{\Delta p_{\text{CO}_2}} = \frac{q_{p,\text{CO}_2}}{A \times \Delta p_{\text{CO}_2}} \quad (1)$$

$$\alpha = \frac{P_{\text{CO}_2}}{P_{\text{N}_2}} \text{ or } \alpha = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} \quad (2)$$

where J_{CO_2} represents CO₂ flux in the unit of m³(STP)/(m² h), Δp_{CO_2} is the trans-membrane CO₂ partial pressure difference (bar) and q_{p,CO_2} is the permeate flow rate of CO₂, in m³(STP)/h, while A is the effective membrane area, m². The unit conversion table of some commonly used gas permeance units is given in Table 1.

2.4. Swelling Capacity Tests. The water swelling capacity of a PVAm, PVA and PVAm/PVA blend was determined by gravimetric analysis. Samples were cast as films in hydrophobic plastic dishes and dried at 45 °C overnight and then 105 °C heat treated for 1 h. The dry samples were humidified in a sealed glass vessel saturated with water vapor at room temperature. The samples were weighed before and after they were swollen by water; the difference between the two masses gave the mass of the swollen water gain. The weight of the sample was recorded after 1 day, and this procedure was repeated until the sample reached a constant weight (equilibrium water uptake). The water swelling degree (SD) of the membranes was calculated according to eq 3

$$\text{SD}(\%) = \frac{W_s - W_d}{W_d} \times 100\% \quad (3)$$

where W_s and W_d are the mass of the swollen and dry membrane materials, respectively.

2.5. Membrane Morphology Characterization. The morphological characteristics of a cross section and surface of the membranes and the selective layer thicknesses were investigated using a field emission scanning electron microscope (FESEM, Zeiss Ultra 55 Limited Edition).

3. MEMBRANE SIZE-UP-SCALING

The coating layers were found to be uneven and the thicknesses very difficult to control when membranes of a larger size were prepared using the simple solution casting method. A dip-coating procedure has therefore been developed to up-scale the preparation of membranes for pilot-scale tests or eventually

industrial-scale applications. The wettability of the solution on the support is a crucial prerequisite in using this method. The coating layer thickness is generally proportional to the volume fraction of polymer in the solution according to the Navier–Stokes equation.¹ When casting pure PVAm aqueous solution on a nonhydrophilic PSf support (the contact angle in the water was 52.4 ± 2.4°),⁴⁸ it was hardly possible to make a continuous and even solution layer due to the high surface tension of the solution on the support surface. However, the hydrophobic groups (–OCCH₃) of the partially hydrolyzed PVA (90+% hydrolyzed) in the PVAm/PVA blend aqueous solution can reduce the surface tension and offer a good contact between the cast solution and the support surface, which enables the formation of the ultrathin coating on PSf support. In this work, the membranes were usually double-coated to ensure a defect-free top layer. The dip-coating vessel (a) and the dip-coating concentration profile¹ (b) are illustrated in Figure 1. The desired thickness of the coating layer was found to be nearly proportional to the concentration of the cast solution, as shown in Figure 2.

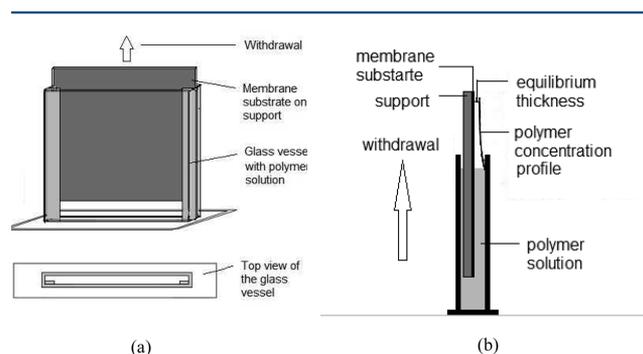


Figure 1. Dip-coating glass vessel (a) and the dip-coating concentration profile (b).

As a comparison, the cross-section SEM images of the membranes prepared from two different procedures are given to illustrate their different membrane microstructures. Figure 3

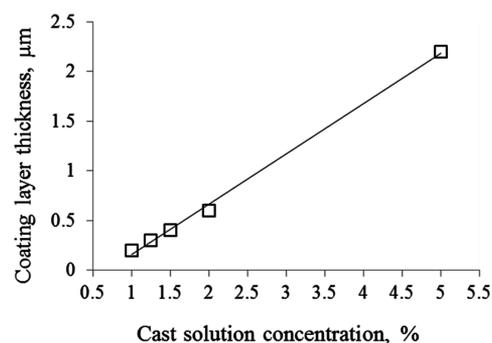


Figure 2. Effect of cast solution concentration on coating layer thickness of the dip-coated membranes.

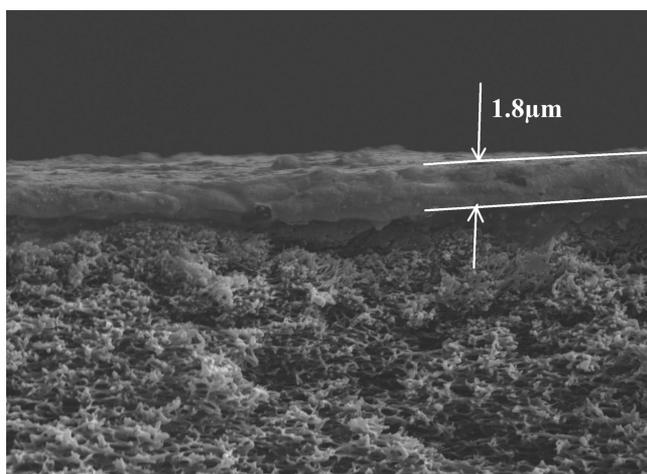
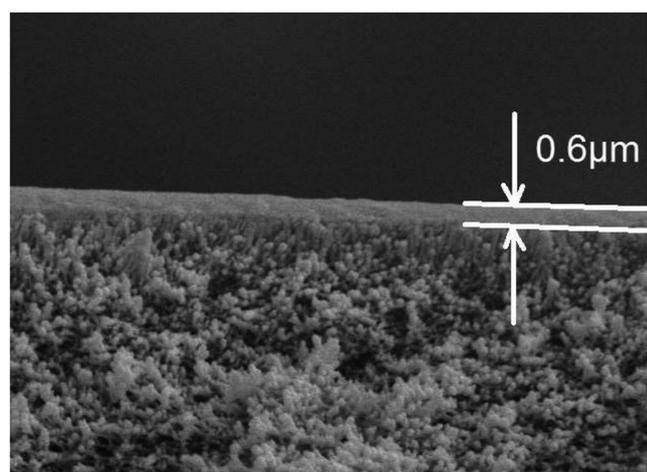
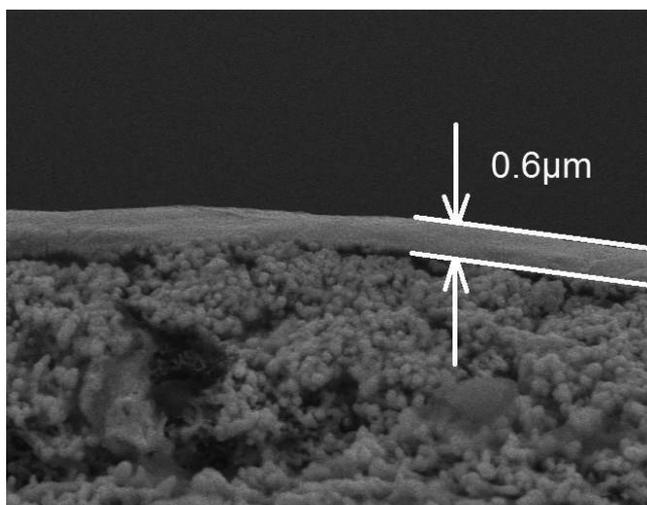


Figure 3. SEM images of membrane cross-section using solution casting.

shows the membrane prepared by solution casting and **Figure 4** presents the membranes by double dip-coating. As we can see, the membranes in **Figure 4** have an evidently denser, more even



(a)



(b)

Figure 4. SEM image of membrane cross section selective layer (double dip-coating) before (a) and after (b) 15 bar test.

and smooth coating layer with much fewer defects, which is believed to arise from the double-coating and vertical evaporation. The defects formed in the first coating were easily covered by the second coating, and hence hardly any defects through the membrane could occur. **Figure 4a** shows a blend membrane selective layer ($0.6 \mu\text{m}$) before testing, and **Figure 4b** is the same membrane after a 15 bar test. No apparent pore-filling was observed from the SEM image after the membrane had been exposed to the high pressure test. The calculated thickness and the observed thickness of the membrane before and after the test were almost the same. The permeation tests confirmed this observation of no material changes when the PVAm/PVA blend membrane was exposed to different feed pressures. Even when exposed to 15 bar pressure, the blended membrane exhibited the same permeation performance before and after, while a pure PVAm membrane prepared with the same PVAm (MW 25 000) could only endure the pressure of less than 5 bar before it suffered a serious loss of gas permeation. The entanglement of the chains of two polymers with different coiling patterns and the strong PVA chain bridging over the pore openings may stop the smaller PVAm chains from leaking into the pores in the substrate support during the preparation and separation processes.

4. RESULTS AND DISCUSSION

4.1. Effect of PVAm Content in Blend. According to Paul,^{49,50} the gas transport properties of a homogeneous blend, X , can be expressed empirically as eq 4⁴⁹

$$\ln X = \Phi_1 \ln X_1 + \Phi_2 \ln X_2 \quad (4)$$

where Φ_i is the volume fraction of component i and X_i represents the gas permeation property, such as permeability and selectivity, of component i . Paul also stated that a homogeneous blend could deviate from this equation positively or negatively, depending on the nature and magnitude of the dynamic interactions between the two polymers. Some blends exhibit strength greater than that of the strongest component.

Experiments showed that the selectivity of the PVAm/PVA blend membrane was a property as such, as can be seen in **Figure 5a**. In the permeation test at 2 bar and 10% CO_2 in feed gas, the blending of 60–80% PVAm with PVA in a membrane resulted in a higher CO_2/CH_4 selectivity than that of the membranes made of either pure PVAm or pure PVA. The selectivity increases with increasing PVAm content in the blend membrane. The membrane with a PVAm content of 67% reached the highest CO_2/CH_4 selectivity of around 45, while the CO_2/CH_4 selectivity of pure PVAm was only 35. The entanglement of the chains of two different polymers with different coiling patterns is believed to bring in a stronger polymeric network, which can avoid too much swelling, and keep the CO_2 facilitated carrier (amino groups) at a relatively higher concentration for a more highly facilitated transport effect.^{51,52} A strong polymeric network can also offer a better sieving effect.

Figure 5b shows the effect of PVAm content on CO_2 permeability. Since the membrane was very swollen during the test, the real thickness in its working condition could hardly be measured. Moreover, the compact effect of a membrane under pressurization may also change the membrane thickness. For a better comparison to optimize the membrane, relative permeability was used by calculating the permeability with a dry membrane thickness, and then normalizing the value with the

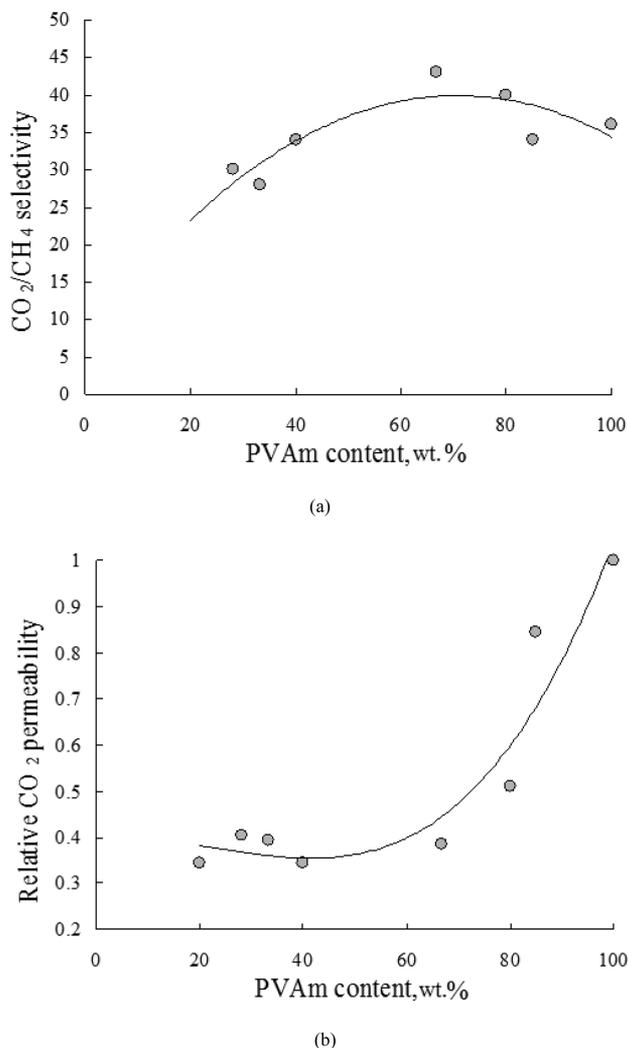


Figure 5. Effect of PVAm content on CO_2/CH_4 selectivity (a) and relative CO_2 permeance (b), at 2 bar, 25 °C.

CO_2 permeability of the 100% PVAm membrane. As can be seen in Figure 5b, a dramatic increase of permeability with an increase of PVAm content occurred when the PVAm content was over 80%. The problem is, however, that this is a low molecular weight PVAm and cannot be prepared as a membrane on a larger scale as already pointed out. CO_2 permeance of the PVAm/PVA membrane with 80% of PVAm is measured to be $0.58 \text{ m}^3/(\text{m}^2 \text{ h bar})$. Each of the tests in Figure 5 was repeated at least three times with the same membrane (an example of the repeated tests is given in section 4.5, Figure 13) and then another two membranes made of the same conditions, and the performance remained nearly the same with an error less than 5%.

Since water contained in the PVAm/PVA blend membrane is involved in the reversible reaction for CO_2 facilitated transport, the swelling capacity of the membrane strongly affects the CO_2 transport and consequently the separation performance, thus the PVAm content must be optimized with respect to the membrane water swelling capacity. The swelling degrees of PVAm/PVA blend samples with varying PVAm content are plotted in Figure 6 as a function of the swelling time at room temperature. The swelling data of pure PVA and PVAm are also included for comparison. As can be seen from the plots in Figure 6, PVAm has the highest degree of swelling, while PVA

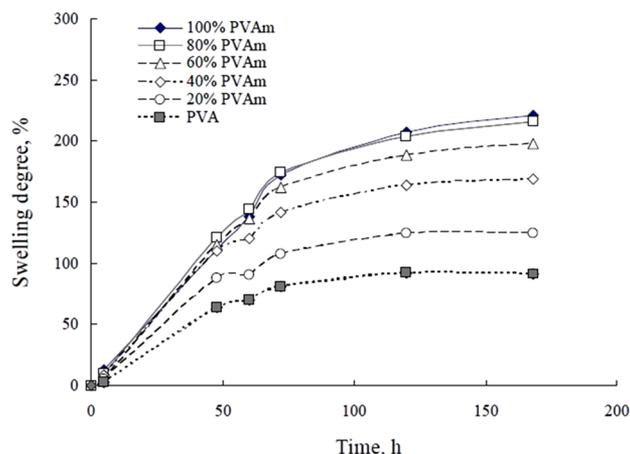


Figure 6. Effect of PVAm content on swelling degree, at room temperature, atmospheric pressure in a water saturated vessel.

has the lowest among all the samples tested, and the degree of swelling of the blends generally increased with an increase of PVAm content in the PVAm/PVA blend. The average degree of swelling of samples with 80% PVAm and 100% PVAm were almost the same. Although the swelling of the pure PVAm sample seems slightly higher after 7 days of humidification, the difference is not significant. However, the pure PVAm sample (MW 25 000) was observed turned into viscous liquid-like, indicating a damage to the polymer network caused by too much swelling after the 7 days' swelling. While all the blend samples showed a clear film, apparently exhibiting a better mechanical property. Considering the balance between CO_2 permeability, CO_2/CH_4 selectivity and the membrane's mechanical strength, a PVAm content of 80% in this PVAm/PVA blend membrane was concluded to be the optimal content, which remained similar to the optimized PVAm content as for CO_2/N_2 separation.

4.2. Effect of Heat-Treatment Conditions. In CO_2 separation using PVAm/PVA blend membranes, the increase of the degree of water swelling was able to bring about both higher CO_2 permeance and selectivity. However, the swelling may result in the loss of the membrane's mechanical strength and sieving effect, as well as diluting the facilitated transport carriers, hence weakening the facilitated transport effect. Cross-linking is an effective and convenient method to reinforce a polymeric membrane matrix, and was used to overcome the overswelling of the PVAm/PVA blend membrane.

Cross-linking can be conducted by the means of chemical reaction, thermal treatment, ion beam, or UV irradiation.^{3,5,50,53} The chemical cross-linking of PVAm with a cross-linking agent, such as NH_4F , glutaraldehyde, H_2SO_4 , HCl, or the combination of these agents was reported, generally by chemical reactions.³⁰ The cross-linking of PVA or PVA blended membranes was widely reported by various cross-linking methods.^{39,54–59} In this work the PVAm/PVA blend membrane was physically cross-linked by heat-treatment to enhance the polymer network, as the chemical reaction between amino groups and cross-linking agents may consume the facilitated transport carriers and therefore reduce the facilitated transport effects.¹ Experiments show that heat cross-linking is effective and practical. The rearrangement of crystal regions and the relaxation and stress of the PVA chain coils resulting from the heat-treatment above the T_g of PVA, enhances the entanglement of the chains of the two blended polymers,

leading to a stronger blend polymer network.^{55,60} The effects of heat-treatment temperature and duration on the swelling capacity of the PVAm/PVA blend sample were discussed in a previously reported work for CO₂/N₂ separation,²⁷ where the optimal cross-linking condition for the maximum swelling capacity with an effective cross-linked network was determined as 105 °C and 1 h.

To optimize membranes prepared by the dip-coating procedure with a focus on CO₂/CH₄ separation at elevated pressures, the effects of heat-treatment of the PVAm/PVA blend membrane on CO₂ permeation were further investigated based on the knowledge gained from the precious study. Figure 7 presents the CO₂ permeance of membranes heat-treated at

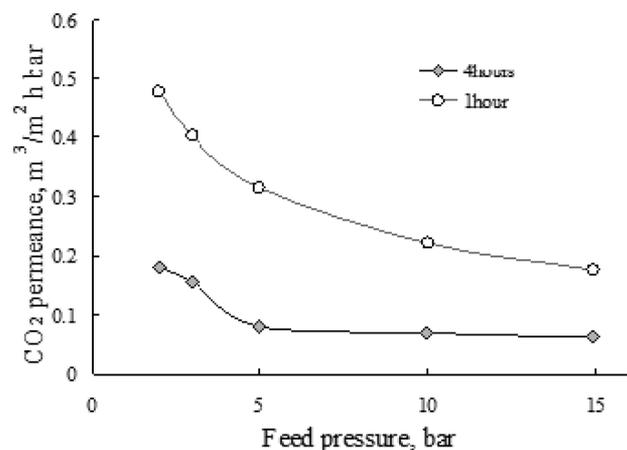


Figure 7. Effect of heat treatment duration on membrane separation performance, selective layer 0.5 μm, at 25 °C, sweep gas flow rate 0.1 mL/s.

105 °C for 1 and 4 h. The other preparation conditions of the two membranes were the same. In Figure 7, it can be seen that at all operation pressures tested (1–15 bar), the CO₂ permeance of the membrane with 4 h of heating was much lower than that of the membrane heated for 1 h, especially at low pressures. A restriction on the chain mobility arising from too much cross-linking of the enhanced polymeric network structure could be the reason, and would lead to a decrease of gas diffusivity. Both membranes showed the tendency of being stable at higher pressures, which is a typical trend found in facilitated transport membranes. However, a longer heating time in the membrane seemed have led to the loss of facilitate transport effect at a relatively lower feed pressure. This indicates that a longer heat treatment time to the membrane is not beneficial to the operation at higher pressures (up to 15 bar).

The CO₂ permeances of PVAm/PVA blend membranes heat cross-linked at 120 and 105 °C for 1 h were plotted as a function of relative humidity at different operation pressures 3, 5, 10, and 15 bar in Figure 8. It can be seen that the membrane being heated at 120 °C exhibited an apparently lower CO₂ permeance at the same operating pressure or same relative humidity compared with that of the membrane being heated at 105 °C. In addition, the CO₂ permeance shows a clear dependence on relative humidity regardless of operation pressures, following exponential relationships similar to the relative humidity, degree of swelling relationship reported in our previous work,⁶¹ and the constants in their exponential trendline equations are considerably difference, as indicated in

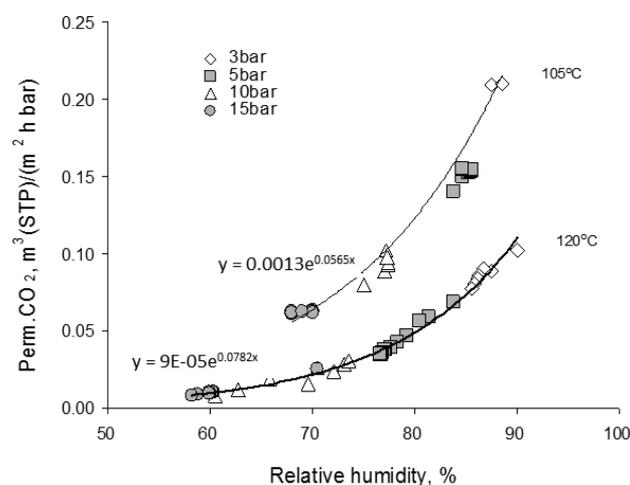


Figure 8. Effect of heat treatment temperature on membrane separation performance, selective layer 0.7 μm, at 25 °C, sweep gas flow rate 0.1 mL/s.

Figure 8. The membrane treated at a higher temperature shows a lower CO₂ permeance at the same relative humidity, and its tendency to increase with the increasing relative humidity is evidently slower, which is in a good agreement with the much smaller pre-exponential factor (A_0) for the membrane treated at 120 °C ($A_0 = 9 \times 10^{-5}$) compared with that of the membrane heated at 105 °C ($A_0 = 1.3 \times 10^{-3}$). A_0 generally reflects the influence of the original structure of the dry polymer network on swelling according to the theory described in literature.^{61,62} The much smaller A_0 suggests that heating at a higher temperature than the optimized temperature may result in an appreciably tighter polymer network, less chain mobility and hence decreased gas diffusivity. Constant B in the exponential equation reflects the sensitivity of the separation performance on relative humidity, depending more on the interaction between gas, water and membrane matrix, including the solubility of gas in water and reactions of gas with water that facilitates the gas diffusion. The difference in B values in the two membranes is much smaller compared with that of the two A_0 values, implying that the interaction between gas, water and membrane matrix should not be very different in both membranes.

From the trends in Figure 8, it can be also seen that the effects of pressure change on the membrane performance are not discernible. It may be due to that the pressure change in the investigated pressure range does not evidently affect the polymer structure (and hence has no notable influence on A_0), but affects the swelling and gas diffusion in the polymer (reflected in constant B), which are not significant and hence overshadowed by the strong effects of feed gas humidity and swelling of the membrane.

To investigate the effect of membrane heat-treatment on CO₂ separation at elevated pressures, the blend membranes were tested with a feed gas containing 35% CO₂ and a feed pressure of up to 16 bar to reach higher CO₂ partial pressures (up to 5.6 bar). In Figure 9a, the CO₂ permeances of the blend membranes heat-treated at 120 and 105 °C are plotted as a function of CO₂ partial pressures. Each of the tests was repeated at least one more time. The average data are reported with an error less than 5%. As expected, the membrane heated at 120 °C exhibited a significantly lower CO₂ permeance (approximately 20% lower) at the same operating pressure

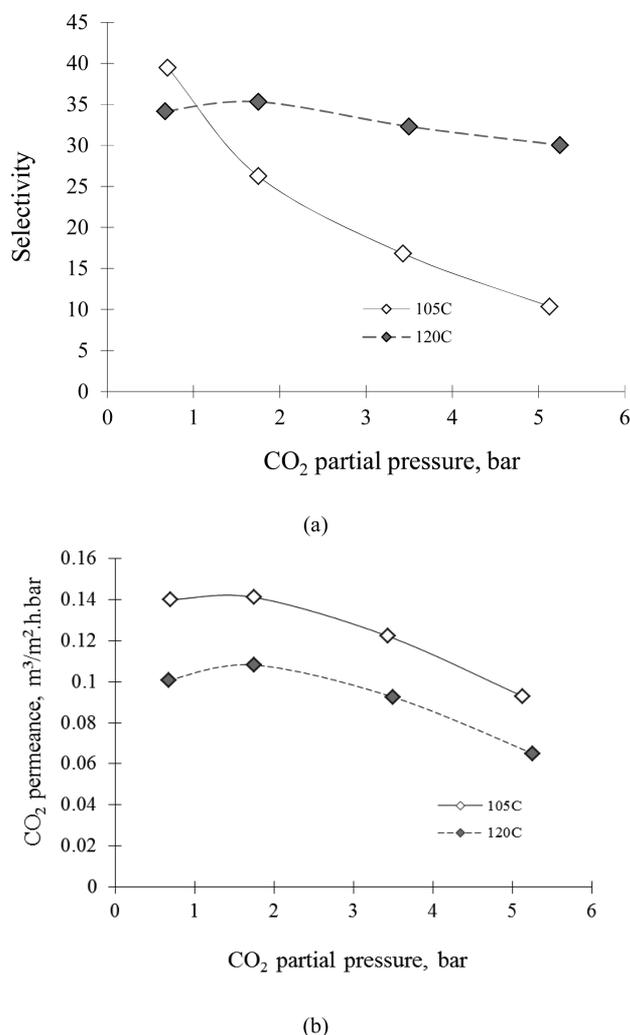


Figure 9. Effects of heat treatment temperature on the blend membranes (a) CO₂ permeance and (b) selectivity at CO₂ partial pressures 0.5–5.6 bar, membrane thickness 0.18 μm .

compared with that of the membrane heated at 105 °C, which again suggests that heating at a higher temperature may result in a relatively “tighter” polymer network, less chain mobility and hence lower gas diffusivity. However, at high CO₂ partial pressures the selectivity of the membrane heated at a higher temperature is higher, as can be seen in Figure 9b, and the higher the pressure, the larger the difference. For applications at elevated pressures (when CO₂ partial pressure is more than 2 bar), the heat-treatment at 120 °C is preferred.

In the “tighter” membrane (heat-treated at 120 °C), permeances of both CO₂ and CH₄ decrease with the increase of CO₂ partial pressure, and the selectivity remains nearly unchanged. The decreases of CO₂ permeance may be due to the saturation of the carriers for the facilitated transport, while the compaction of the membrane at higher pressure also contributes to the decrease of the gas permeation of both gases, especially the CH₄ permeation. Whereas in the membrane heat-treated at a lower temperature, a dramatic fall in CO₂/CH₄ selectivity appears, implying an increase of the CH₄ permeance at higher pressures. This is believed resulted from the more competitive plasticization (swelling) by CO₂ and water against the compaction, and hence the partial loss of the sieving function in this less heat-treated membrane at higher pressures.

It should be noted that in this PVAm/PVA blend membrane, the CO₂ separation performance, especially CO₂ permeance, evidently decreases with the increase of separation pressures. The reduced membrane swelling capacity due to the compact polymer network (tighter membrane) can partly explain this phenomenon, but the facilitated transport effect also contributes significantly to the decreased separation performance because of the saturation of the CO₂ facilitated transport carriers at high pressures.

4.3. Effect of Selective Layer Thickness. As a rule of thumb, a composite membrane with a thinner dense coating layer is generally more gas permeable, therefore a thin and defect-free selective layer is normally preferred for a composite membrane in order to achieve a high gas permeation rate. In facilitated transport membranes, however, the selective layer thickness cannot be optimized by simply reducing the coating layer thickness. A thicker selective layer may offer more facilitated transport carriers or favor the complexation reaction over diffusion and, therefore, result in a better separation performance, especially when high pressure separation is considered. Ideally, an optimized thickness can be calculated, as suggested by Schultz,⁶³ who related the optimized thickness with the ratio between the carrier complexation reaction rate in the facilitated transport membranes and the Fickian diffusion rate using the second Damköhler number, $l^2/(D \cdot t_{0.5})$, in which l is the membrane thickness, D is the diffusion coefficient of the free solute, and $t_{0.5}$, half time of the complexation reaction. The term D/l^2 can be considered as the diffusion time constant. At high Damköhler number, $l^2/(D \cdot t_{0.5}) \gg 1$, the reaction is very fast and the transport of the free component can be neglected. If the Damköhler number is low, or $l^2/(D \cdot t_{0.5}) \ll 1$, there will be no facilitated transport effect and the Fickian diffusion of the free component is rate-determining in the process. The Damköhler number gives the ratio of characteristic reverse reaction to diffusion times, which can be used to estimate the degree of the facilitated effect in a transport. This theory has been employed in the current work as a guideline for the optimization of the coating layer thickness, but only qualitatively, because of the lack of accurate data on membrane thickness and gas diffusion in a swollen state. Nevertheless, experiments show the trends of the separation performance changing with CO₂ partial pressures, which supports this theory. A thicker membrane provided a better separation performance for the separation of CO₂/CH₄ at elevated pressures, as shown in Figure 10, where the CO₂ permeance (a) and selectivity of CO₂/CH₄ (b) of two PVAm/PVA blend membranes with respective coating layer thicknesses of 0.18 and 0.5 μm are plotted as the function of CO₂ partial pressure.

Generally, gas permeance in a membrane decreases proportionally to the increase of the selective layer thickness. In facilitated transport membranes selective layer thicknesses also make differences in selectivity, especially when feed CO₂ partial pressure is low, as being reported in our previous work for CO₂/N₂ separation,²⁷ in which the comparison of the performance at low pressures gives a clear trend, showing that thinner membranes have much higher CO₂ permeance and selectivity over other unreactive gases, but become less selective at higher pressures. In this work, however, we only tested membrane performance at elevated pressures (partial pressure >0.5 bar) in view of the biogas separation conditions. Because of experimental convenience for larger-size membrane fabrication, we only studied membranes of two thicknesses, that is, 0.18 μm (dip-coated with 1 wt % polymer solution) and

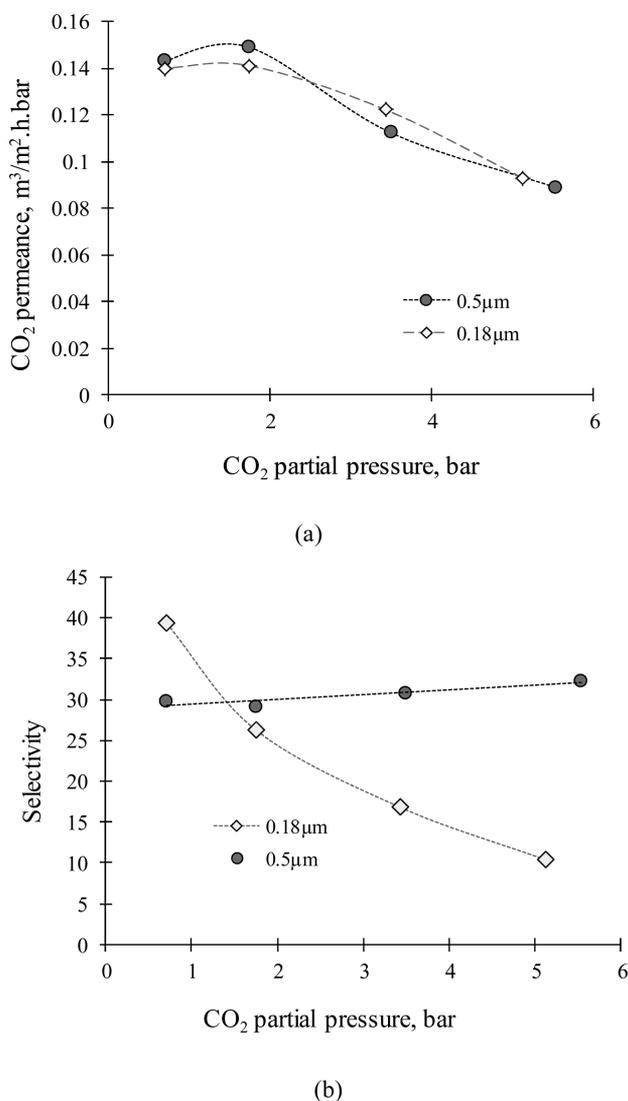


Figure 10. Effects of coating layer thickness on (a) CO₂ permeance and (b) CO₂/CH₄ selectivity, at CO₂ partial pressures 0.5–5.6 bar.

0.5 μm (with 2 wt % solution). Surprisingly, two membranes of different selective layer thickness in this study have quite comparable CO₂ permeance in the investigated range (1.4–16 bar with 35% CO₂ in feed stream, or CO₂ partial pressure 0.5–5.6 bar), and the CO₂ permeances of both membranes decrease with increasing partial pressure, as indicated in Figure 10a. The competition and balance between diffusion (thinner membrane favors it) and facilitated transport (thicker membrane with more carriers favors it) in the two membranes may explain this phenomenon. For instance, in the thinner membrane, the carriers may be not sufficient to complex with the excessive CO₂ at a CO₂ partial pressure over 0.5 bar and lose the facilitated transport effect. However, as shown in Figure 10a, membranes are very different when selectivity is concerned. The thin membrane ($l = 0.18 \mu\text{m}$) exhibits a higher selectivity of CO₂/CH₄ at low pressures (when CO₂ partial pressure is less than 1.5 bar), but the selectivity decreases dramatically when CO₂ partial pressure increases. The selectivity drops to 10 when CO₂ partial pressure increases to 5.0 bar, which can no longer provide an efficient CO₂/CH₄ separation. In the thicker membrane ($l = 0.5 \mu\text{m}$ in Figure 10), however, the CO₂/CH₄ selectivity even slightly increases when CO₂ partial pressure

increases from 0.5 to 5.6 bar. The selectivity decreasing with the increase of CO₂ partial pressure in the thinner membrane can be explained by the loss of facilitated transport effect due to the saturation of the facilitated carrier sites at higher CO₂ partial pressures, and the more significant plasticization effect, which favors the transport of “inert” gases (CH₄ in this case), and CO₂/CH₄ selectivity therefore increases. The membrane with a thickness of 0.5 μm seems having sufficient carriers against the plasticization effect for a CO₂ partial pressure of up to 5.6 bar. For higher pressures, the optimized membrane could be thicker. Further work needs to be done to optimize membrane thickness if higher pressures are applied.

4.4. Selection of Support. A porous support substrate must be used to provide mechanical strength to the thin selective layer, while obtaining a high gas permeance in a composite membrane. The properties of different membrane layers of a composite membrane influences the gas transport through the membrane according to the so-called “resistance-in-series” theory.^{5,64} There are two layers that mainly contribute to membrane resistance in a composite membrane; the selective top layer and the microporous skin layer of the support substrate, both expressed as the thickness of the respective layer divided by permeance (l/p_i). Hence, the overall gas transport resistance can be calculated by the addition of resistance from the different paths.⁵ This theory suggests that the thickness of the selective layer, the material, pore size, and pore size distribution of the porous support layer determine the overall gas transport resistance, which indicates that attention should be paid not only to tailoring the coating layer thickness, but also to using a larger pore-size porous support with material that favors CO₂ transport.

Five different support materials including PSf, cellulose acetate (CA) and polyacrylonitrile (PAN) were previously investigated as support for the PVAm composite membrane.³⁰ They suggested that a difference of (>20 000) between the average molecular weight (MW) of PVAm and the molecular weight cutoff (MWCO) of the support material should be a prerequisite to obtaining an effective PVAm layer, and hence a PSf support membrane (MWCO 20 000) was the optimal support material.³⁰

Since most of the applications for the CO₂/CH₄ separation are at elevated pressures, to increase the CO₂ permeance and provide mechanical strength for higher pressure operations has been set as the goal in the selection of the support substrate. PSf ultrafiltration membranes are used as the support for the PVAm/PVA blend membranes based on the our previous study. The effects of the morphology in PSf supports are therefore the main focus. SEM images of the cross section of the PSf ultrafiltration membranes of MWCO 20 000 (a) and MWCO 50 000 (b) provided by Alfa Laval are presented in Figure 11, showing the finger type (a) and sponge type (b) asymmetric structures, respectively. The sponge type is obviously more suitable as support for high pressure operations considering that the weak sections in the finger type support may collapse at high pressures. The surface images of the PSf ultrafiltration membranes of MWCO 20 000 (c) and MWCO 50 000 (d) are also given for a comparison of the surface porosity. The PSf membrane of MWCO 50 000 has larger openings and higher porosity on the surface, which should lead to lower transport resistance if the pores are not blocked during membrane coating.

In this work, judging from the SEM images of the membrane coatings on porous supports (for example Figure 3 and Figure

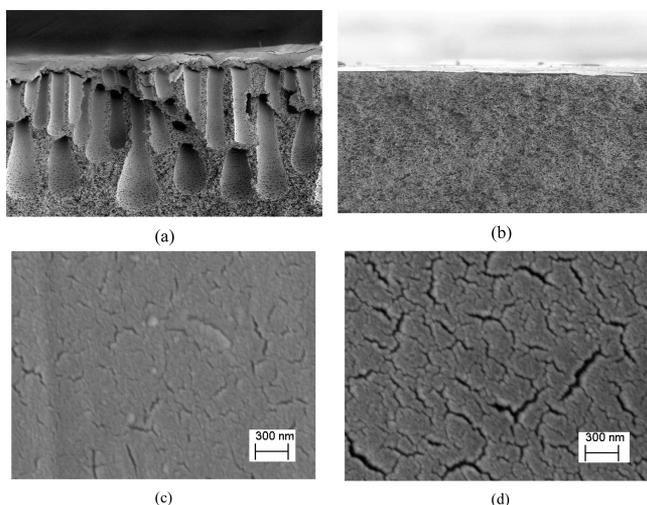


Figure 11. SEM images of (a) cross-section of PSf membrane (MWCO 20 000) with finger type and (b) PSf (MWCO 50 000) with sponge type; SEM images of (c) surface of PSf membrane (MWCO 20 000) and (d) PSf membrane (MWCO 50 000).

4), the clearly formed coating layers of PVAm/PVA blend membrane were obtained without pore-filling when casting the blend solution of PVAm (MW 25 000) and PVA (MW 75 000) on PSf support (MWCO 20 000 and 50 000). The average molecular weight of this blend was 35 000. It seems that the difference between polymer molecular weight (MW) and support pore size (MWCO) suggested in³⁰ is not required to form an effective selective layer in this case: this may possibly be due to the strong entanglement of the PVAm and PVA polymer chains of different coiling patterns. The PSf UF membrane (MWCO 50 000) with sponge type asymmetric structures was therefore chosen as the support membrane for further development of the composite blend membrane. The separation performances reported in this paper are all of membranes cast on PSf supports of MWCO 50 000. Gas permeation tests were first performed on the PSf support membrane without the coating layer, and the results showed that the support with a higher MWCO exhibited higher gas permeance (as expected) due to the difference in the resistance of gas transport through the pores of different sizes partially filled with condensed water from the humid feed gas. The CO₂ permeances through PSf of MWCO 20 000 and MWCO 50 000 were 0.2 ± 0.05 m³ (STP)/(m² h bar) and 0.4 ± 0.05 m³ (STP)/(m² h bar), respectively, which are lower than that of their coated counterparts with eliminated or at least reduced water condensation. The washing procedure of the support may introduce some difference to the performance of the support, since contaminants in the support membrane affected the gas transport through the supports and, to a certain extent, the tendency of water condensation, hence the PSf support membrane had to be rinsed to remove any possible contaminants.

4.5. Aging Effect and Membrane Stability. The aging effect of the PVAm/PVA blend membrane was investigated with a gas permeation test using the single gases CO₂ and CH₄, so the interaction between the gases would not hide the influence of the membrane aging on the permeation of different gases. The aged membrane had been cut from the same piece of a large membrane and kept in a dry atmosphere at room temperature for 18 days while its counterpart was tested. The

gas permeances of the membranes with and without aging were plotted in a logarithm as a function of relative humidity as in Figure 12. It can be seen that the trends of the CO₂ permeance

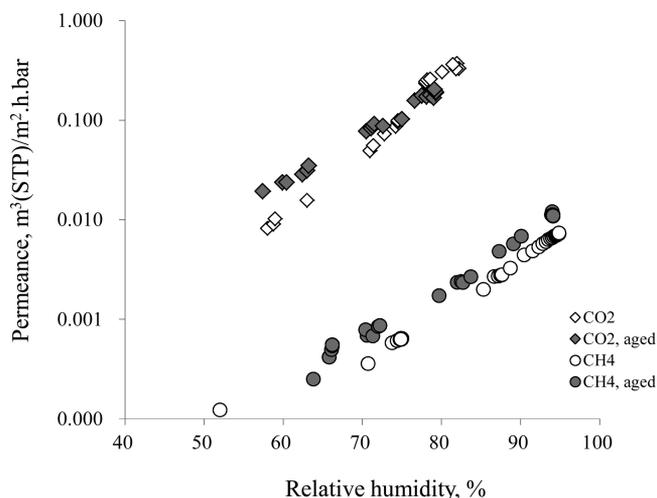


Figure 12. Effect of aging on CO₂ and CH₄ gas permeance, selective layer thickness 0.5 μm, at 2 bar, 25 °C, aged over 18 days.

increase with an increase of relative humidity in the two membranes are similar. The two plots nearly overlapped, except that the aged membrane only reached 0.2 m³ (STP)/(m² h bar) at the relative humidity of around 80%, lower than 0.36 m³ (STP)/(m² h bar) of the new membrane at the relative humidity of 83%.

However, contrary to the quickly aged membranes stored directly in the ambient atmosphere, the PVAm/PVA blend membranes stored under humidified conditions or humidified before being stored in the ambient atmosphere did not show evident aging effects. The humidified pretreated membranes were found to be more stable and no aging effects were observed. Figure 13 shows a 5 times repeated test of a membrane in 10 days. After it was humidified and tested, the membrane was repeatedly run in the same conditions 5 times and remained with the same separation performance. CO₂ permeances in 6 runs almost overlapped and exhibited the same

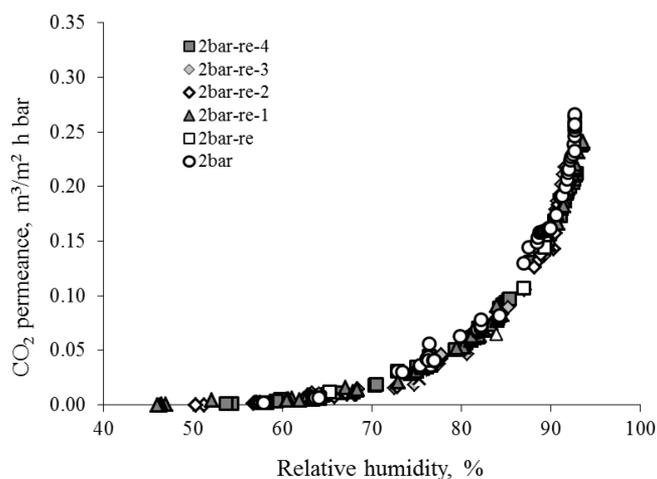


Figure 13. Effect of relative humidity on CO₂ permeance, selective layer 0.3 μm, PVAm/PVA ratio: 4, at 25 °C, 2 bar, sweep gas flow at 0.1 mL/s.

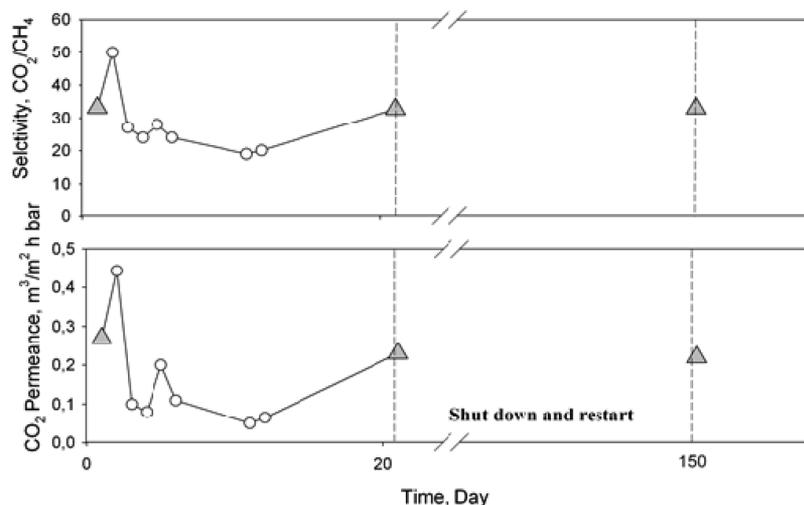


Figure 14. Stability of the PVAm/PVA blend membrane over 5 months.

trend as with the effect of relative humidity. This figure further confirms the repeatable permeance of the membranes presented in this paper.

The stable CO_2/CH_4 separation permeance of a PVAm/PVA blended membrane in a 5-month test can also be found in Figure 14. The data reported in this system shows an average error less than 5%. During a 20-days test, by pressurizing the feed gas from 2 to 20 bar and then down to 2 bar again, the membrane performed quite similarly in similar operation conditions, as shown in Figure 14 with triangles, which stand for operation at 2 bar, 25 °C and with a sweep flow of 0.1ml/s. This suggests that the compact polymeric network caused by pressurization (as described in section 3) is reversible. After operating at a higher pressure, the membrane performance can be recovered when the pressure is reduced and other parameters are restored. The last 2 triangles were the restarted test of the membrane cell after 20 days running and then being stored in atmospheric conditions for 4 and a half months; no aging effect was recorded. A reversible, humidity-induced phase transition during the swelling process of the hydrogel membrane material may be one reason for the antiaging effect and hence the long-term stability of the humidified pretreated membranes. The mechanism of the humidification treatment is beyond the scope of this work and not further discussed in this paper.

5. CONCLUSION

Important progress has been made in the preparation of the PVAm/PVA blend membrane with respect to CO_2/CH_4 separation performance and long-term stability with a potential for industrial-scale applications. The pressure range tested in the current work was 2–16 bar. The factors which affect membrane separation performance were investigated and optimized. A pretreated PSf ultrafiltration membrane of MWCO 50 000 was selected as the support substrate. The up-scaling of the preparation of the flat sheet blend membrane to small pilot scale is practical and simple. The CO_2 permeance up to $0.58 \text{ m}^3(\text{STP})/(\text{m}^2 \text{ h bar})$ and the selectivity of CO_2/CH_4 up to 45 were documented by using the optimized PVAm/PVA blend FSC membranes. No significant aging of the membrane was found when being stored in an ambient atmosphere after the treatment with humidity. A good stability of the membrane was documented over a five-month test.

Further optimization of the blend membrane for higher pressures (up to 80 bar) is ongoing.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: deng@nt.ntnu.no.

*E-mail: hagg@nt.ntnu.no.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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