High-molecular-weight polyvinylamine/piperazine glycinate membranes for CO₂ capture from flue gas

Yuanxin Chen and W.S. Winston Ho *

William G. Lowrie Department of Chemical and Biomolecular Engineering,

Department of Materials Science and Engineering,

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

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

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

Abstract

High-molecular-weight polyvinylamine (PVAm)/piperazine glycinate (PG) membranes were successfully synthesized for CO₂/N₂ separation from flue gas. PVAm with different molecular weights was synthesized through free radical polymerization by adjusting the monomer concentration and initiator amount. The synthesized PVAm showed both a higher molecular weight and a higher solution viscosity than the commercially available PVAm (Lupamin[®] 9095 from BASF Corporation). The high viscosity of the PVAm solution at a low concentration allowed the preparation of much thinner membranes. It could also help reducing penetration of the polymer solution into the pores of the substrate, further reducing the mass transfer resistance. Consequently, a high CO₂ permeance could be obtained from thin membranes with the thickness of 100 – 200 nm. In the membrane, PVAm acted as the fixed-site carrier for CO₂ facilitated transport whereas PG was incorporated into the PVAm polymer matrix and served as the mobile carrier. The PVAm/PG blend solution was coated onto different substrates including polyethersulfone (PES) and polysulfone (PSf) substrates. Sodium dodecyl sulfate (SDS) surfactant was incorporated in the coating solution to improve the adhesion between the membrane layer and the substrate in some cases. The resultant PVAm/PG membranes exhibited a high CO₂ permeance of about 1100 GPU and a high CO₂/N₂ mixed gas selectivity of more than 140 at the typical flue gas temperature of 57°C along with 17% water vapor.

Keywords: High-molecular-weight polyvinylamine; Piperazine-glycinate; Facilitated transport membrane; CO₂ capture from flue gas

1. Introduction

Electricity generation through conventional coal combustion is well-developed. However, the large amount of carbon dioxide (CO₂) emission from this conventional technology has become a main reason for greenhouse gas driven climate change. Therefore, carbon capture from flue gas has become an important solution to the global warming problem. Conventional carbon capture technologies include absorption processes using amine-based solvents, adsorption processes employing solid adsorbents, and cryogenic distillation. However, many barriers exist when applying these technologies, including high capital cost, large footprint, numerous operational concerns, and high energy penalty for CO₂ stripping and regeneration of sorbents. On the other hand, membrane separation becomes more promising due to its low energy consumption, small footprint, low cost and easy operation.

There are two main challenges for CO₂ capture from flue gas. First, there is a large amount of flue gas to be treated. For example, a 600 MW coal-fired power plant could generate flue gas at a rate of 500 m³/s [1]. Second, the flue gas contains only 12% to 14% CO₂ at one atmosphere, which means the driving force for CO₂ separation is relatively low (< 0.15 atm). To overcome these challenges, both a high CO₂ permeance and a high CO₂/N₂ selectivity are required for a CO₂-selective membrane. A high CO₂ permeance can help to reduce the membrane area, and further reduce the capture cost. A high CO₂/N₂ selectivity can help to obtain a high CO₂ purity with low energy consumption [2,3].

For the two main components, CO₂ and N₂, in flue gas (where CO₂ is the more permeating component), the CO₂ permeance and the **ideal** CO₂/N₂ selectivity of a membrane are defined as follows [4]:

$$\text{CO}_2 \text{ permeance} = \frac{P_{\text{CO}_2}}{l} = \frac{J_{\text{CO}_2}}{(p_{f\text{CO}_2} - p_{p\text{CO}_2})} \quad (1)$$

$$\text{CO}_2/\text{N}_2 \text{ ideal selectivity} = \alpha_{\text{CO}_2/\text{N}_2} = \frac{P_{\text{CO}_2}}{P_{\text{N}_2}} \quad (2)$$

where $\frac{P_{\text{CO}_2}}{l}$ is the CO_2 permeance, and the common unit is the gas permeation unit (GPU), 1 GPU = $10^{-6} \text{ cm}^3(\text{STP})/(\text{s} \cdot \text{cm}^2 \cdot \text{cmHg})$. J_{CO_2} is the flux of CO_2 , P is the permeability of CO_2 , l is the selective layer thickness of the membrane, $p_{f_{\text{CO}_2}}$ and $p_{p_{\text{CO}_2}}$ are the partial pressures of CO_2 in the feed and permeate sides, respectively. $\alpha_{\text{CO}_2/\text{N}_2}$ is the **ideal** CO_2/N_2 selectivity, which is defined as the permeability ratio between CO_2 and N_2 . **The ideal selectivity is applicable when the permeate partial pressure is much smaller than the feed partial pressure.**

The state-of-the-art PolarisTM membranes from Membrane Technology and Research (MTR) Inc. for CO_2 capture from flue gas have shown high CO_2 permeances of 1000 – 3000 GPU [1,5,6]. However, the PolarisTM membranes show low CO_2/N_2 selectivities of 20 – 50, which are governed by the Robeson upper bound for the solution-diffusion membranes [7,8]. On the other hand, facilitated transport membranes can provide a much higher CO_2/N_2 selectivity (100 – 1500) due to the reversible reaction between CO_2 and reactive amino group-containing carriers in the membrane [9-21]. In this work, facilitated transport membranes were synthesized with polyvinylamine (PVAm) as the fixed-site carrier and piperazine glycinate (PG) as the mobile carrier. Since the CO_2 permeance is affected adversely by the membrane thickness according to Equation (1), a higher CO_2 permeance can be obtained with a lower membrane thickness. To achieve a lower thickness of the membrane, a polymer matrix with a higher molecular weight is advantageous. First of all, it can provide a stronger polymer matrix for the membrane. Second, with a higher molecular weight, a higher viscosity of the polymer solution can be achieved even at a low solution concentration. Furthermore, the high viscosity can help reducing penetration of the coating solution into the pores of the substrate, further **reducing** the mass transfer resistance

of CO₂ transport through the membrane. Overall, with the high-molecular-weight PVAm, a high CO₂ permeance can be expected from the membrane.

In this work, high-molecular-weight PVAm was synthesized to obtain thin membranes with high CO₂ permeances. According to the literature [20-23], PVAm can be synthesized by free-radical polymerization. For free-radical polymerization, the molecular weight of the polymer increases with higher monomer concentration and lower initiator concentration [24,25]. In this work, various monomer concentrations and initiator amounts were used to obtain PVAm with different molecular weights. After the synthesis of PVAm, the aminoacid salt PG was incorporated into the polymer solution to serve as the mobile carrier, which could enhance the mobility of the CO₂-carrier reaction product. The PVAm/PG coating solution was coated on top of different substrates including polysulfone (PSf) and polyethersulfone (PES). In some cases, the adhesion between the coating solution and the substrate was not good. Therefore, sodium dodecyl sulfate (SDS) as the surfactant was incorporated into the coating solution to improve the adhesion between the amine solution and the substrate, and to **reduce** the defects of the membrane. In our previous work, the effects of different aminoacid salts on membrane transport performance were investigated, and PG was found to perform better than other mobile carriers including potassium glycinate and lithium glycinate [26].

2. Experimental

2.1. Materials

Glycine (98.5%), piperazine (99%), *N*-vinylformamide (NVF, 98%), α,α' -azodiisobutyramidine dihydrochloride (AIBA, 97%), sodium dodecyl sulfate (SDS, 99%), and isopropanol (IPA, 99.9%) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, Certificated ACS Plus) and ethanol (99.5%) were purchased from Fisher Scientific. Strong base

anion-exchange resin (Purolite[®] A600OH) was kindly donated by Purolite Corporation (Bala Cynwyd, PA). All the chemicals were used as received without further purification.

Biomax polyethersulfone ultrafiltration substrate (Biomax PES) with a molecular weight cut off of 300 kDa was purchased from EMD Millipore (Billerica, MA). The Biomax PES substrate was soaked in deionized water for overnight and then in IPA for 30 min to remove the glycerol in the pores before usage. Another kind of PES substrate (Lab-fabricated PES) was fabricated in our lab by a phase-inversion technique with controlled pore size and porosity. The NL polysulfone substrate (NL PSf) was kindly provided by NL Chemical Technology, Inc. (Mount Prospect, IL). TriSep polysulfone substrate (TriSep PSf) was purchased from TriSep Corporation (Goleta, CA). All the substrates had a similar structure, which contained a porous PES or PSf layer on top of a nonwoven polyester fabric. The surface morphologies including the average pore size and the porosity of the four substrates are listed in Table 1. The pore size and porosity of the substrates were determined by using Clemex Vision Professional Edition (Longueuil, Quebec, Canada) software to analyze the SEM surface images of the substrates taken by FEI Nova NanoSEM400 (FEI Company, Hillsboro, OR).

Table 1. Surface morphologies of different polymer substrates.

Polymer Substrate	Average Pore Size (nm)	Porosity (%)
Biomax PES	72.0	15.0
Lab-fabricated PES	68.0	16.0
NL PSf	12.1	5.3
TriSep PSf	10.0	8.0

2.2. Synthesis of PVAm

High-molecular-weight PVAm was synthesized following the route shown in Fig. 1. NVF as the monomer was first purified by vacuum distillation to remove any inhibitor. Then, purified NVF was added in water to form solutions with different monomer concentrations. The solution in a 250 mL 3-neck round-bottom flask under nitrogen protection was preheated to 50°C in a water bath. AIBA as the initiator at a predetermined initiator/monomer ratio was added to the solution. Then, the polymerization was carried out under nitrogen at 50°C for 3 h. After the polymerization, the polymer solution was transferred to a 2 M HCl aqueous solution to carry out the acidic hydrolysis at 70°C for 5 h. Subsequently, the polymer solution was poured into a large amount of ethanol (ethanol/polymer solution volume ratio = 4/1) for precipitation. The obtained polymer was dried in a vacuum oven at 60 °C for 48 hours. Then, the dry polymer was dissolved in water with reflux at 60°C for overnight to form a 3 wt.% solution. Strong base anion-exchange resin was added to the polymer solution for ion-exchange. Finally, vacuum filtration was used to remove the resin after the pH of the polymer solution reached 10.

Fig. 1. Synthesis route of high-molecular-weight PVAm.

2.3. Synthesis of PG mobile carrier

The mobile carrier of the aminoacid salt PG was synthesized by the following procedure. First, glycine was dissolved in water to form a 17.5 wt.% solution and stirred for 2 h at room temperature. Then, piperazine at the stoichiometric amount was added to react with glycine to form the aminoacid salt. The reaction took place at room temperature for 2 h, and then the homogeneous PG mobile carrier solution was obtained.

2.4. Membrane preparation

After the syntheses of both PVAm and PG, the PG mobile carrier solution was incorporated into the PVAm solution with a 65/35 PG/PVAm weight ratio, which formed the so-called coating solution. In some cases, 5 wt.% SDS surfactant in the total solid composition was added to the coating solution to improve the adhesion between the solution and the substrate. The PVAm/PG membrane was prepared by a knife-coating method. On top of different flat-sheet substrates, the coating solution was coated using a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap setting. The empirical equation (Equation (3)) was used for controlling the thickness of the dry membrane by adjusting the gap setting of the coating knife.

$$l \times \rho_{dry} = 0.5 \times c \times \rho_{solution} \times l_{gap} \quad (3)$$

where l (μm) is the dry PG/PVAm membrane thickness, ρ_{dry} (g/cm^3) is the density of the dry PVAm/PG membrane, $\rho_{solution}$ (g/cm^3) is the density of the coating solution, c (by weight) is the total solid concentration of the coating solution, and l_{gap} (μm) is the gap setting of the coating knife. After the coating, the membrane was dried in a fume hood at room temperature for overnight before testing. The chemical structures of the components in the resultant membrane, including PVAm, PG and SDS, are shown in Fig. 2. The structure of the PVAm/PG membrane is shown schematically in Fig. 3. As can be seen from Fig. 3, the polymer substrate contains a nonwoven fabric, which provides the mechanical strength to the membrane, and a porous PES or PSf layer. A thin amine layer containing PVAm and PG was coated on top of the substrate.

Fixed-site carrier:

Polyvinylamine (PVAm)

Mobile carrier:

Piperazine glycinate (PG)

Surfactant:

Sodium dodecyl sulfate (SDS)

Fig. 2. Chemical structures of PVAm, PG and SDS.

Fig. 3. Schematic of PVAm/PG membrane structure.

2.5. Gas transport performance measurements

Gas transport performance measurements were conducted by using a gas permeation apparatus as shown in Fig. 4, which was modified from a set-up described in a previous paper [11]. First, the PVAm/PG membrane was loaded into a stainless-steel rectangular permeation cell with an effective membrane area of 2.7 cm^2 . Then, the membrane cell was placed in a temperature-controlled oven (Bemco Inc. Simi Valley, CA). The oven temperature was set at 57°C , which is the typical flue gas stream temperature. The simulated flue gas containing 20% CO_2 and 80% N_2 was used as the feed gas at a flow rate of 60 cc/min, and argon was used as the sweep gas at a flow rate of 30 cc/min. Both the feed gas and sweep gas were humidified when each passing through 150 mL water in a 2 L stainless-steel humidifier (Swagelok, Westerville, OH) filled with 60% (by volume) packing of glass Raschig rings. After leaving the humidifier, 17% (by volume) water content was achieved at 57°C for each of the feed gas and sweep gas. Then, both gas streams passed through the respective second stainless-steel vessels to reduce any liquid water entrainment before reaching the membrane cell. Each of the second stainless steel vessels with a 500 mL volume contained no water, and it was filled with 60% (by volume) packing of glass Raschig rings. A countercurrent flow configuration was used through the membrane cell to offer the maximum driving force. After leaving the cell, water vapor in both streams was knocked out in two respective condensers. The testing pressures were adjusted by the two near-ambient pressure regulators. The feed side pressure was set at 1.5 psig, and the sweep side pressure was set at 1.0 psig. The outlet gas compositions of both retentate and permeate streams were analyzed by using a gas chromatograph (GC) equipped with thermal conductivity detectors (TCDs) (Agilent Technologies, Palo Alto, CA). SUPELCO Carboxen[®] 1004 micropacked GC column (Sigma-Aldrich, St. Louis, MO) was used for the GC analysis.

CO₂ permeance and CO₂/N₂ selectivity were determined from the GC analysis to characterize the membrane transport performance.

Fig. 4. Schematic of the permeation apparatus for gas transport performance measurements. 1 and 2: water reservoirs; 3 and 4: water pumps; 5 and 6: mass flow controllers; 7 and 8: humidifiers; 9 and 10: second vessels with packing; 11: the gas permeation cell with membrane inside; 12: oven; 13 and 14: water knockout vessels; 15 and 16: near-ambient pressure regulators; 17 and 18: pressure gauges; 19 and 20: needle valves; 21: GC.

In this work, 57°C was used as the testing temperature for most cases. However, 102°C was also used to investigate membrane separation performance at the high temperature, which will be discussed in Section 3.6.

2.6. Characterization of PVAm and membrane properties

The chemical structure of the synthesized PVAm was characterized by Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectroscopy using a Nicolet 470 Fourier transform infrared spectrometer (Thermo Electron Co., Waltham, MA). The viscosity of the 3 wt.% PVAm solution was measured using a Brookfield Digital Viscometer DV-E (Brookfield Engineering Laboratories, Inc., Middleboro, MA). The weight average molecular weight of the synthesized PVAm was characterized by dynamic light scattering (DLS) using Zetasizer Nano ZS (Malvern Instruments Inc., Westborough, MA). The cross-section morphology of the synthesized membranes was observed by scanning electron microscopy (SEM) using FEI Nova NanoSEM400 (FEI Company, Hillsboro, OR).

3. Results and discussion

3.1. FTIR characterization of synthesized PVAm

The FTIR spectrum of the synthesized PVAm is shown in Fig. 5. The strong and wide absorption band between 3500 cm^{-1} and 3200 cm^{-1} was considered to be the stretching vibration peaks of primary amine groups [27-31]. The peak at 2950 cm^{-1} was assigned to the stretching vibration absorption of C-H bond. The peak at 1580 cm^{-1} was attributed to the bending vibration absorption of N-H bond of the primary amine groups. The peak at 1650 cm^{-1} should be attributed to the stretching vibrations of C=O bond in amide groups, indicating that the acidic

hydrolysis was not complete, which means that there were still some amide groups which had not been transformed to amino groups.

Fig. 5. FTIR spectrum of the synthesized PVAm.

3.2. Effects of PVAm synthesis conditions on polymer molecular weight and polymer solution viscosity

As mentioned, PVAm with a higher molecular weight was advantageous for the membrane transport performance. First, PVAm provides the mechanical strength as the polymer matrix of the membrane, which means a stronger and more stable membrane will be obtained from a higher molecular weight polymer. Second, with higher molecular weight, the polymer solution will be more viscous at the same concentration, and the adhesion between the coating solution and the substrate will be better. This can help to maintain a good CO₂/N₂ selectivity of the membrane. Moreover, higher viscosity can also help to reduce the penetration of the polymer

coating solution into the pores of the substrate, which can further reduce the mass transfer resistance and improve the CO₂ permeance of the membrane.

In this work, PVAm samples with different molecular weights were synthesized through free radical polymerization by adjusting the monomer concentration and the initiator amount (or initiator/monomer weight ratio). Fig. 6 shows the correlation between the 3 wt.% polymer solution viscosity and the synthesis conditions including the monomer concentration and the initiator/monomer weight ratio. At the same polymer solution concentration (3 wt.%), a higher viscosity indicated that the synthesized polymer had a higher molecular weight. From Fig. 6, it can be seen that with higher monomer concentration, the viscosity of the polymer solution was higher than that with lower monomer concentration at the same initiator/monomer weight ratio. In this work, 50 wt.% monomer concentration was also used for the polymerization. However, the reaction took place too fast, and there was gel formation during the polymerization. Another trend which can be seen from Fig. 6 is that the PVAm solution viscosity increases with a lower initiator/monomer weight ratio. However, when the initiator/monomer weight ratio was less than a certain amount ($\sim 0.14\%$ at 30 wt.% and 40 wt.% monomer concentration; $\sim 0.11\%$ at 45 wt.% monomer concentration), there was a significant reduction of the polymer solution viscosity. It could be due to the fact that the initiator concentration was too low, so that it was difficult to initiate the polymerization reaction, which led to a lower molecular weight of the polymer.

Fig. 6. Correlation between the 3 wt.% PVAm solution viscosity and the synthesis conditions including monomer concentration and initiator/monomer weight ratio.

In this work, two main types of the synthesized PVAm were used to prepare membranes. The weight average molecular weights of synthesized PVAm (a) and PVAm (b) were measured by DLS, which were 719,000 and 1,200,000, respectively. The synthesis conditions, the viscosities of 3 wt.% polymer solutions and the molecular weights of the two polymers are listed in Table 2. To compare the synthesized PVAm with the commercially available PVAm, the viscosity of 3 wt.% polymer solution and the molecular weight of Lupamin[®] 9095 (from BASF Corporation) are also listed in Table 2. As can be seen, the synthesized PVAm showed a much higher molecular weight than Lupamin[®]. Besides, the viscosity of the 3 wt.% synthesized PVAm solution was significantly higher than that of 3 wt.% Lupamin[®] solution. Moreover, Lupamin[®] was obtained by basic hydrolysis using sodium hydroxide, therefore a large amount of

byproduct (about 66 wt% sodium formate salt) was formed in the polymer product, which can damage the stability of the membranes due to the salting-out problem. In contrast, since acidic hydrolysis was used instead of basic hydrolysis in this work, no byproduct was formed. All of these factors indicated that the high-molecular-weight PVAm synthesized in this work was very much advantageous for the membrane transport performance compared to the commercially available Lupamin[®] product.

Table 2. Comparison of the PVAm synthesized in this work and commercially available Lupamin[®] 9095 product.

Polymer	Monomer Concentration (wt.%)	Initiator/Monomer Ratio (by weight)	Viscosity of 3 wt.% Polymer Solution (cp)	Weight Average Molecular Weight
PVAm (a)	30	0.5/100	486	719,000
PVAm (b)	40	0.14/100	1,400	1,200,000
Lupamin [®]	N/A	N/A	50	340,000

3.3. Membrane morphology via SEM

SEM was used to observe the cross-section morphology of the membrane. The SEM image in Fig. 7 shows the cross-section of the PVAm/PG membrane prepared on top of the lab-fabricated PES substrate. The membrane was prepared using PVAm (b) with a molecular weight of 1,200,000. The composition of the membrane was 35/65 (weight ratio) PVAm/PG. As can be seen, the thin PVAm/PG layer with a thickness of around 150 nm was successfully coated on top of the substrate. The sponge-like structure underneath the amine layer was the nanoporous PES layer. The nonwoven fabric, which provides the mechanical strength to the PES substrate, cannot be seen from this image with this particular magnification.

Fig. 7. SEM cross-section image of the PVAm/PG membrane on top of the lab-fabricated PES with a membrane thickness of ~ 150 nm.

3.4. *Effect of SDS surfactant on membrane separation performance*

During our initial attempts, no surfactant was introduced in the membrane composition. However, due to the poor adhesion between the PVAm/PG solution and the substrate, some defects were formed in the thin membrane layer, which caused a low CO_2/N_2 selectivity. The Millipore Biomax PES substrate was an exception, which will be discussed in Section 3.5. To improve the adhesion between the membrane layer and the substrate, and to **reduce** the defects, SDS surfactant with an amount of 2 – 10 wt.% in total solid membrane composition was incorporated in the coating solution.

One interesting observation was that after the incorporation of SDS surfactant, there was an increase of the coating solution viscosity. The effect of the SDS amount on the coating solution

viscosity is shown in Fig. 8. The coating solution with a different SDS amount had a total solid concentration of 10 wt.% with a PG/PVAm weight ratio of 65/35. The PVAm used here was the one with molecular weight of 719,000. Without SDS, the coating solution had a viscosity of 450 cp. After the incorporation of 2, 5, 8 and 10 wt.% SDS surfactant in the total membrane solid composition, the coating solution viscosity increased to 630, 812, 830 and 835 cp, respectively. The viscosity increase with the SDS surfactant was mainly due to the interaction between the anionic SDS surfactant and the amino groups [32,33]. However, when the SDS amount was more than 5 wt.% in the total solid composition, phase separation in the coating solution was observed frequently, which could lead to a low CO₂/N₂ selectivity of the membrane.

Fig. 8. Influence of SDS amount on coating solution viscosity.

Fig. 9 shows the effect of SDS amount on the membrane transport performance including the CO₂ permeance and the CO₂/N₂ selectivity. All the membranes shown in Fig. 9 were prepared

with a thickness of ~ 150 nm coated on the lab-fabricated PES substrate. As can be seen, without SDS surfactant in the composition, the membrane showed a CO_2/N_2 selectivity of only 87. After the incorporation of 2 wt.%, 5 wt.% and 8 wt.% SDS surfactant in the total solid membrane composition, the selectivity increased to 117, 154 and 160, respectively. At least three membrane samples were tested for each composition, and the selectivity error bars for the tested samples of these three compositions were ± 7 , ± 10 and ± 10 , respectively. This indicated that SDS surfactant successfully improved the adhesion between the coating solution and the PES substrate. The selectivity was lower with 10 wt.% SDS in the total solid, which was mainly due to the phase separation after the introduction of too much amount of SDS. The phase separation in the coating solution could lead to minor defects in the amine layer and further reduce the CO_2/N_2 selectivity.

Fig. 9. Influence of SDS surfactant amount on membrane transport performance.

It can also be seen from Fig. 9 with permeance error bars that the permeance differences among 0%, 2% and 5% SDS were within the experimental errors. However, when the SDS amount was more than 5 wt.% in the total solid membrane composition, there was a decline of CO₂ permeance, presumably owing to the phase-separation problem and carrier-concentration dilution caused by the excessive SDS addition. Therefore, 5 wt.% SDS surfactant was used for most cases in this work, and it improved the adhesion between the amine layer and the substrate significantly.

It should be brought up here that for the PVAm with even higher molecular weight (1,200,000), no surfactant was needed to obtain a good CO₂/N₂ selectivity of the membrane. This was due to the high viscosity of the coating solution from the high molecular weight of the polymer, which provided a good adhesion between the amine solution and the substrate. More work will be done with higher molecular weight PVAm in the future.

3.5. *Effect of substrate on membrane separation performance*

As mentioned, different substrates were used for the preparation of amine-containing membranes in this work. Table 3 shows the comparison of membrane transport performances with different substrates. As can be seen, the membrane on the Biomax PES from Millipore showed the best performance. Besides, no SDS surfactant was needed for this case. The reason was that the Biomax PES was more hydrophilic compared to the other three substrates, which provided a good adhesion to the coating solution. Due to the good adhesion, a thin membrane layer (~ 100 nm) could be coated on top of the substrate without any defects. Subsequently, both a high CO₂ permeance and a high CO₂/N₂ selectivity could be achieved from this substrate. In contrast, for the other three substrates, when the membrane layer was less than 150 nm, defects could be introduced to the membrane, resulting in a lower CO₂/N₂ selectivity.

Table 3. Comparison of membrane transport performances on different substrates.

Polymer Substrate	SDS Amount in Total Solid (wt.%)	Estimated Amine Layer Thickness (nm)	CO ₂ Permeance (GPU)	CO ₂ /N ₂ Selectivity	CO ₂ /N ₂ Selectivity Error Bar
Biomax PES	0	100	1100	290	±30
Lab-fabricated PES	5	150	930	154	±10
NL PSf	5	150	768	132	±7
TriSep PSf	5	150	690	123	±5

Although the Biomax PES provided the best membrane performance, the high cost of this substrate was a limitation for further scale-up fabrication of the membrane. Therefore, the other three alternative substrates were investigated. As is shown in Table 3, the membrane prepared on TriSep PSf and NL PSf substrates showed lower CO₂ permeances. This could be due to the smaller pore size and lower porosity in the PSf substrates (as shown in Table 1), which contributed more mass transfer resistance to the membrane. The CO₂/N₂ selectivity was also lower on the PSf substrates, which could be explained by the fact that the PSf was more hydrophobic than PES substrates. Overall, the lab-fabricated PES was a better option due to the relatively good membrane separation performance and low cost.

3.6. Effect of *temperature along with water vapor content* on membrane separation performance

In this work, 57°C was used as the membrane testing temperature for most cases as it is the typical flue gas temperature. At this temperature, the saturated water vapor content in the gas phase was about 17%. However, 102°C along with a water content of 80% on the feed side was also used to investigate the membrane performance at the high temperature. The two membranes shown in Table 4 were prepared with the same condition. PVAm with 719,000 molecular weight was used to prepare the membranes, and 5 wt.% SDS was incorporated in the total solid membrane composition. Both membranes were prepared on the lab-fabricated PES substrate with an estimated membrane thickness of 180 nm. As can be seen, at 102°C, the membrane showed a much higher CO₂ permeance, which was more than 1800 GPU. The main reason for the high performance was that the reactivity of the amine carriers was higher at the higher temperature. Besides, the mobility of both mobile carriers and the CO₂-carrier reaction products was also improved at the higher temperature. Moreover, the higher water content at the higher temperature could also help to improve the separation performance based on the facilitated transport mechanism, by which water enhances the amine-CO₂ reaction.

Table 4. Test conditions for gas permeation measurements.

Temperature (°C)	Water content		CO ₂ Permeance (GPU)	CO ₂ /N ₂ Selectivity
	Feed	Sweep		
57	17%	17%	843	142
102	80%	57%	1815	175

Although the membrane performed better at 102°C than at 57°C, it can introduce more operational cost due to the higher water amount required at the higher temperature. Besides, 57°C and 17% water content are the typical flue gas conditions after the flue gas desulfurization

(FGD) in coal-fired power plants. Therefore, 57°C was used in this work for most cases. The feasibility of using 102°C as the operational temperature needs further investigation.

3.7. Advantage of using high molecular weight PVAm to prepare thinner membranes

Table 5 shows the comparison of membrane separation performances with different PVAm molecular weights. The last four membranes shown in Table 5 were prepared using a pilot-scale continuous coating machine in Dr. Ho's group at The Ohio State University (OSU). As can be seen from the first 4 membranes in this table, the lab-scale membranes and scale-up membranes showed a similar transport performance as they had the same membrane thickness of 180 nm. In other words, with the same membrane thickness, the transport performances of PVAm (a) and (b) membranes can be considered similar due to the experimental error of ± 30 GPU for CO₂ permeance and ± 10 for CO₂/N₂ selectivity. However, there was an obvious difference on the CO₂/N₂ selectivity when the membrane thickness was thinner, i.e., 155 nm. As can be seen, the selectivity of the membrane was only 115 for PVAm (a) (MW 719,000) compared to 148 for PVAm (b) (MW 1,200,000). This can be explained by the fact that with a lower molecular weight and at the same solution concentration, the viscosity of the solution was not high enough to provide a good adhesion to the substrate. Therefore, the main advantage of the high-molecular-weight PVAm is that it allowed the preparation of a much thinner defect-free membrane with higher CO₂ permeance, which is a result of a higher solution viscosity even at the same low concentration. Fig. 10 shows two SEM cross-sectional images of the pilot-scale amine membranes with the different thicknesses.

Table 5. Comparison of membrane separation performances with different PVAm molecular weights (membranes were prepared using 3 wt.% polymer concentration and 35/65 PVAm/PG composition).

Polymer	PVAm Molecular Weight	Pilot-scale/Lab-scale	Amine Layer Thickness (nm)	CO ₂ Permeance (GPU)	CO ₂ /N ₂ Selectivity
PVAm (a)	719,000	Lab-scale	180	734	136
PVAm (b)	1,200,000	Lab-scale	180	750	145
PVAm (a)	719,000	Pilot-scale	180	710	152
PVAm (b)	1,200,000	Pilot-scale	180	751	155
PVAm (a)	719,000	Pilot-scale	155	764	115
PVAm (b)	1,200,000	Pilot-scale	155	823	148

(a) Amine thickness of ~155 nm.

(b) Amine thickness of ~180 nm.

Fig. 10. SEM cross-sectional images of pilot-scale amine membranes with (a) ~155 nm prepared using MW 1,200,000 PVAm and (b) ~180 nm using MW 719,000 PVAm.

Lupamin[®] membranes were also prepared to make a comparison with the high-molecular-weight PVAm membranes. However, with the same solution concentration, it was difficult to prepare a thin membrane (100 – 200 nm) without defects. In other words, the Lupamin[®] membranes showed a very low CO₂/N₂ selectivity (5 – 10). This further indicated the advantage of using high-molecular-weight PVAm to prepare thinner membranes with higher CO₂ permeances.

Another potential advantage of the higher PVAm molecular weight is that due to the more stable polymer matrix, a higher amount of mobile carriers can be introduced to the membrane, which can lead to higher membrane separation performance. The study of incorporating more mobile carriers in the membrane will be carried out separately.

3.8. Stability of PVAm/PG membrane

Fig. 10 shows the 20-h stability test results of the PVAm/PG membrane on the Biomax PES substrate with an average CO₂ permeance of 1100 GPU and a CO₂/N₂ selectivity of 290. Fig. 11 depicts the 20-h stability test results of the PVAm/PG membrane on the lab-fabricated PES substrate with an average CO₂ permeance of 920 GPU and a CO₂/N₂ selectivity of 160. It can be seen that the performance of both membranes was stable over the 20-h tests. No sign of performance degradation was observed for either CO₂ permeance or CO₂/N₂ selectivity. The stable and good separation performance indicated that the synthesized PVAm/PG membrane was promising for the application of CO₂ capture from flue gas [26,34].

The membrane stability in the presence of SO₂ and O₂ was also investigated. Our initial results from the laboratory test using a simulated flue gas comprising 16% CO₂, 64% N₂, 17% H₂O, 3% O₂, and 3 ppm SO₂ showed that the PVAm/PG membrane in its spiral-wound module exhibited a 200-h stable CO₂ permeance (~ 580 GPU) and CO₂/N₂ selectivity (~ 200) [35]. In a

recent 200-h test using a real flue gas consisting of approximately 10% CO₂, 67% N₂, 6% O₂, 17% H₂O, 0.5 – 5 ppm SO₂, and 1.5 – 4 ppm NO₂, which was attained after the SO₂ polishing step of the Department of Energy baseline document [36], at the National Carbon Capture Center in Wilsonville, AL, the PVAm/PG membrane in 3 spiral-wound modules showed stable performance with respect to the SO₂ and NO₂. The details of the spiral-wound module fabrication and performance will be published in the near future.

Fig. 11. Stability of PVAm/PG membrane on Biomax PES substrate.

Fig. 12. Stability of PVAm/PG membrane on lab-fabricated PES substrate.

4. Conclusions

High-molecular-weight PVAm/PG membranes were successfully synthesized. PVAm with a higher molecular weight compared to the commercial PVAm (Lupamin[®]) was synthesized as the fixed-site carrier, and PG was incorporated as the mobile carrier to the membrane composition. SDS surfactant was incorporated to the coating solution to improve the adhesion between the coating solution and the substrate. Membranes with a thickness of 100 – 200 nm were coated on different substrates. The resultant membranes showed a CO₂ permeance up to 1100 GPU and a CO₂/N₂ selectivity of more than 140 at 57°C with 17% water vapor. The membranes showed a stable result during the 20-h stability tests. The high-molecular-weight PVAm/PG membrane

synthesized in this work showed a great potential for the application of CO₂ separation and capture from flue gas.

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Nomenclature

c	concentration of coating solution
J	gas flux
J_{CO_2}	flux of CO ₂
l	membrane thickness
l_{gap}	gap setting of the coating knife
P_{CO_2}	permeability of CO ₂
P_{N_2}	permeability of N ₂
p	pressure

p_f pressure on the feed side of the membrane

p_p pressure on the permeate side of the membrane

p_{fCO_2} CO₂ partial pressure on the feed side of the membrane

p_{pCO_2} CO₂ partial pressure on the permeate side of the membrane

Greek letters

α selectivity

α_{CO_2/N_2} selectivity of CO₂ over N₂

ρ_{dry} density of the dry amine-containing polymer membrane

$\rho_{solution}$ density of coating solution

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