New Pebax[®]/zeolite Y composite membranes for CO₂ capture from flue gas

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Abstract

A new Pebax[®]/zeolite Y composite membrane with three layers on top of the polyethersulfone (PES) substrate was designed and successfully synthesized for CO₂ capture from flue gas. The three layers were the zeolite Y inorganic layer, selective Pebax[®] layer, and polydimethylsiloxane (PDMS) cover layer, respectively, from bottom to top. Zeolite Y with a particle size of about 40 nm was synthesized and deposited onto the PES substrate. On top of the zeolite Y layer, a selective polymer layer was deposited with the blend solution of Pebax[®] and ethylene oxide (EO)-containing small molecules. A PDMS cover layer was applied on top of the Pebax[®] layer for defect abatement. The composite membrane showed a better CO₂/N₂ separation performance compared to the membrane without the zeolite Y layer, which was due to two reasons. First, the hydrophilic zeolite Y layer improved the adhesion between the Pebax[®] polymer layer and the substrate, which allowed for the preparation of much thinner and defect-free membranes. Second, the zeolite Y layer had a smaller interparticle pore size than the PES substrate and then minimized the penetration of polymer solution into the pores, which reduced the mass transfer resistance of CO₂ molecules through the membrane. The effects of different Pebax[®] blend compositions and various coating conditions on the membrane separation performance were also investigated. This work for the first time reports a thin Pebax[®] membrane with a high CO₂ permeance and a relatively good CO₂/N₂ selectivity at 57°C. The resulting Pebax[®]/zeolite Y composite membrane exhibited a CO₂ permeance up to 940 GPU and a CO₂/N₂ mixed gas selectivity of 30 at 57°C, indicating promising potential for CO₂ capture from flue gas.

Keywords: CO₂-selective membrane; Polymer/zeolite composite membrane; Pebax[®]; Zeolite Y; Ethylene oxide group

1. Introduction

Carbon dioxide separation and capture from flue gas streams has been widely believed to be the most important solution to greenhouse gas driven climate change. Compared to conventional CO₂ separation methods including solvent absorption, solid adsorption and cryogenic distillation, membrane separation is a more promising method due to its system compactness, energy efficiency, operational simplicity and kinetic ability to overcome the thermodynamic solubility limitation [1-3].

Polymer membranes and inorganic membranes are two major categories of CO₂ separation membranes. Gas transport through most of the polymer membranes follows the solution-diffusion mechanism (Fig. 1(a)), which is based on both the solubility of gases in the membrane and the diffusivity of gases through the membrane. Most of the recent work on the polymeric solution-diffusion membranes has focused on copolymers which generally have a hard (glassy) polymer segment such as polyamide (PA) or polyester and a soft (rubbery) polymer segment such as polyethylene oxide (PEO) [4]. The hard segment provides the mechanical strength to the membrane, while the soft segment interacts with CO₂ molecules for enhanced transport. Solution-diffusion polymer membranes usually suffer from a trade-off between permeability and selectivity, which can be represented by the Robeson upper bound for the membrane performance [5]. Recent work has shown that solution-diffusion polymer membranes such as the PolarisTM membrane from Membrane Technology and Research, Inc. (USA) and the ultra-thin Polyactive[®] membrane from GKSS Research Centre Geesthacht GmbH (Germany) have the potential to achieve high CO₂ permeances (1000 – 2000 GPU) [6-8], but the selectivity was limited by the Robeson upper bound, which was usually below 30 at 57°C (flue gas temperature).

Fig. 1. Schematics of CO₂/N₂ transport mechanisms through polymer and inorganic membranes.

Pebax[®] 1657 copolymer contains 60 wt.% PEO and 40 wt.% polyamide 6 (PA6), the structure of which is shown in Fig. 2. In this copolymer structure, PEO acts as the soft segment and provides the CO₂-philic property, while PA serves as the hard segment and provides the film-forming ability and mechanical strength to the membrane. Yave et al. reported that Pebax[®] 1657 had a CO₂ permeability of around 175 Barrers and a CO₂/N₂ selectivity of 32 at 50°C [9].

Although permeability is one of the most widely used parameters for membranes, it can only represent the property of a certain membrane material, while the permeance is the one used for carbon capture system design and cost analysis. For industrial applications, no matter how high the permeability is, a thick membrane can reduce the permeance significantly and increase the membrane area, and further increase the capture cost. Although researchers did a lot of work on

Pebax[®] membranes, they usually reported CO₂ permeabilities for thick membranes [10-19], while very few reported high CO₂ permeances for thin membranes (< 2 μm). Car et al. reported that a Pebax[®]/PEG blend composite membrane of less than 2 μm showed a CO₂ permeability of 122 Barrers at 30°C [20]. Liu et al. reported a CO₂ permeance of around 350 GPU and a CO₂/N₂ selectivity of 35 for a thin Pebax[®] 2533 membrane with a thickness of 0.7 μm at 25°C [21,22].

Fig. 2. Chemical structures of Pebax[®] 1657, PEG and PEG-DME.

Inorganic membranes for CO₂/N₂ separation are microporous and have a different transport mechanism compared to solution-diffusion membranes. The CO₂/N₂ separation from microporous inorganic membranes depends on both molecular sieving and surface diffusion (Fig. 1(b)). The similar size of CO₂ (3.3 Å) and N₂ (3.64 Å) molecules indicates that achieving a CO₂ rich permeate by the simple molecular sieving is not very effective. Surface diffusion,

particularly in combination with the molecular sieving, then becomes a main factor for the separation. In microporous inorganics such as zeolite Y (with a pore size of 7.4 Å and a Si/Al ratio of 1.5 – 3.8), CO₂ favorably adsorbs and diffuses along the surface wall, providing a high CO₂ permeance as well as a high CO₂/N₂ selectivity in combination with the molecular sieving. The performances of such membranes approach or cross the upper bound set by polymer membranes. Recent literatures have shown that zeolite membranes on an inorganic substrate, such as alumina, showed a CO₂ permeance of around 2000 – 3500 GPU and a CO₂/N₂ selectivity of around 30 – 500 at room temperature [23-26]. Although these inorganic membranes have shown higher separation performances compared to polymer membranes, it is very difficult to fabricate defect-free inorganic layers reproducibly. Besides, due to the fact that the inorganic substrates are thick, brittle, expensive and not amendable to continuous fabrication, the scale-up of inorganic membranes is complicated and costly.

This work for the first time designs a Pebax[®]/zeolite Y composite membrane with three layers for CO₂/N₂ separation (Fig. 3). Zeolite Y with a particle size of about 40 nm was synthesized and successfully deposited onto the PES substrate. A thin Pebax[®] layer was then coated on top of the zeolite Y layer. The inorganic zeolite Y layer not only improved the adhesion between the polymer layer and the substrate, but also had a smaller pore size than the PES substrate, which could improve the CO₂ permeance by reducing the penetration of the polymer solution into the pores underneath. A PDMS cover layer was coated on top to cover any possible defects of the thin Pebax[®] layer. To our best knowledge, this work for the first time reports such a composite membrane with a Pebax[®] layer thickness of less than 500 nm, showing a high CO₂ permeance (~ 940 GPU) while maintaining a good CO₂/N₂ selectivity (~ 30) at 57°C.

Fig. 3. Schematic of Pebax[®]/zeolite Y composite membrane structure.

2. Experimental

2.1. Materials

Poly(ethylene glycol) with an average molecular weight of 200 (PEG200), poly(ethylene glycol) dimethyl ether with an average molecular weight of 500 (PEG-DME500), heptane (99%), isopropanol (IPA, 99.9%), Ludox HS-30 colloidal silica (SiO₂, 30%), aluminum isopropoxide (Al(O-CH(CH₃)₂)₃, 98%), and tetramethylammonium bromide ((CH₃CH₂CH₂)₄N(2Br), 98%) were purchased from Sigma-Aldrich. Tetramethylammonium hydroxide ((TMA)₂O(2OH), 25% aqueous) was purchased from SACHEM Inc. (Austin, TX). Ethanol (99.5%) was purchased from Fisher Scientific. Pebax[®] 1657 was kindly donated by Arkema Inc. (King of Prussia, PA). PDMS with a trade name of Dehesive[®] 944 and its corresponding crosslinker (Wacker[®] Crosslinker V24) and catalyst (Wacker[®] Catalyst OL) were kindly provided by Wacker Silicones, Inc. (Adrian, MI). All the chemicals were used as received without further purification.

Biomax[®] PES ultrafiltration membrane substrate with a molecular weight cut-off of 300 kDa (PES300, flat sheet substrate with a ~ 100 µm PES layer on top of a ~ 200 µm non-woven fabric) was purchased from EMD Millipore (Billerica, MA). The average pore size of the PES substrate was around 72 nm, and the porosity was about 15%. The PES300 substrate was soaked in deionized water for overnight and then in IPA for 30 min to remove the glycerol in the pores before usage.

2.2. Zeolite Y synthesis

Nano zeolite Y with a 40 nm average diameter was synthesized using the method reported in the literature [27]. The gel composition (molar ratio) was: 0.048 Na₂O : 2.40 (TMA)₂O(2OH) : 1.2 (TMA)₂O(2Br) : 4.35 SiO₂ : 1.0 Al₂O₃ : 249 H₂O, where TMA⁺ is the tetramethylammonium cation.

Silicon and aluminum sources were prepared separately before mixing. For the silicon source, 26.2 g Ludox HS-30 and 10.46 g TMAOH were mixed and stirred at room temperature for 30 min. For the alumina source, 12.5 g aluminum isopropoxide was dissolved in the mixture of 76.5 g H₂O and 52.3 g TMAOH while stirring at 70°C in a water bath until the suspension became clear. Then, 11.3 g TMABr was added to the aluminum source. After mixing the silicon and aluminum sources, the clear sol was aged at room temperature with stirring for 3 days, followed by stirring for 4 days at 100°C.

After the hydrothermal treatment, the product was isolated by dialysis and ultracentrifugation. Isolated zeolite Y particles were washed with distilled water until pH = 7 and ion exchanged by stirring the zeolite suspension in a 0.1 M NaCl solution overnight. The ion exchanged product was washed with deionized water and stored as a 1 wt.% aqueous dispersion.

2.3. Membrane preparation

The polymer/zeolite Y (ZY) composite membrane was synthesized following three steps to form the structure with three layers (Fig. 4). Zeolite Y was first deposited onto the PES300 substrate using a vacuum-assisted dip deposition method [28]. Basically, the zeolite Y dispersion in water was dip deposited onto the PES substrate with the help of a vacuum applied on the backside of the PES substrate. The substrate with the zeolite Y layer was then kept in a humidity chamber with a relative humidity of ~ 60% to prevent the zeolite Y layer from forming cracks before the coating of the Pebax[®] layer.

Fig. 4. Schematic of the preparation procedure of the Pebax[®]/zeolite Y composite membrane.

The Pebax[®] layer was prepared with a Pebax[®] blend solution consisting of ethylene oxide (EO)-containing small molecules using a spin-coating method. Pebax[®] 1657 was first dissolved in a 70/30 (weight ratio) ethanol/water mixture solvent to form a 3 wt.% solution with stirring under reflux at 80°C for overnight. Then, PEG200 or PEG-DME500 at a predetermined amount was incorporated into the solution. The weight ratio of Pebax[®]/PEG200 was 50/50, and the weight ratio of Pebax[®]/PEG-DME500 was 25/75. After that, a more amount of 70/30 ethanol/water solvent was added to form a solution with a total solid concentration of 2 wt.%. The solution was stirred at room temperature for 1 hour. Finally, the solution was spin-coated onto the zeolite Y layer on top of the PES substrate using a WS-650 spin-coater (Laurell Technologies, North Wales, PA). The spinning speed for coating the Pebax[®] layer was kept at 3000 rpm for 1 minute.

After the coating of the Pebax[®] layer, the membrane was placed in a hood at ambient temperature for around 6 hours to allow all the solvent to evaporate. Then, a PDMS cover layer was coated on top to cover any defects of the selective Pebax[®] layer. The PDMS solution with a concentration of 1.5 wt.% (in heptane solvent, PDMS/crosslinker/catalyst weight ratio of 100/1/0.5) was spin-coated on top of the selective layer. The spinning speed for PDMS coating was kept at 6000 rpm for 1 minute. After the coating, the membrane was kept in a hood for 2 h and then kept in an oven at 100°C for 0.5 h to evaporate the solvent and to complete the crosslinking of PDMS.

2.4. Gas transport performance measurements

Gas transport performance measurements were conducted by using a gas permeation apparatus described in a previous paper [29]. The synthesized composite membrane with an effective membrane area of 3.4 cm² was loaded into a small rectangular permeation cell. A countercurrent flow configuration was applied to offer the maximum driving force across the membrane. A binary gas mixture containing 20% CO₂ and 80% N₂ on dry basis was used as the feed gas. The flow rate of the dry feed gas was 60 cc/min, and the pressure on the feed side was kept at 1.5 psig. The flow rate of the argon sweep gas was 30 cc/min, and the sweep pressure was kept at 1.2 psig. The cell was loaded inside of a temperature-controlled oven (Bemco Inc. Simi Valley, CA) and the testing temperature was kept at 57°C, which was the average flue gas temperature. After leaving the gas permeation cell, the gas compositions of both retentate and permeate gas streams were analyzed by a gas chromatograph (GC) equipped with thermal conductivity detectors (TCDs) (Agilent Technologies, Palo Alto, CA). The GC column used was the SUPELCO Carboxen[®] 1004 micropacked type (Sigma-Aldrich, St. Louis, MO). The test was conducted under the dry condition, and no water was introduced to the system.

The effect of water vapor on the membrane transport performance was also investigated. For the test with the existence of water, all the other testing conditions were the same, except that both the feed gas and the sweep gas were humidified by passing through 100 mL water in a 500 mL stainless steel humidifier (Swagelok, Westerville, OH) filled with 60% (by volume) packing of glass Raschig rings, to achieve the saturation water content of 17% at 57°C.

Based on the transport measurement, CO₂ permeance and CO₂/N₂ selectivity were calculated to characterize the membrane transport performance. The CO₂ permeance indicates a measure on the flux of CO₂ through the membrane, and the CO₂/N₂ selectivity shows the separation of CO₂ over N₂. The definitions of the CO₂ permeance and the CO₂/N₂ selectivity are shown below [30].

$$\frac{P_{CO_2}}{l} = \frac{J_{CO_2}}{(p_{f_{CO_2}} - p_{p_{CO_2}})} \quad (1)$$

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \quad (2)$$

J_{CO_2} is the flux of CO₂, P is the permeability, l is the selective layer thickness of the membrane, $p_{f_{CO_2}}$ and $p_{p_{CO_2}}$ are the feed and permeate pressures of CO₂, respectively. The CO₂ permeance is defined as $\frac{P_{CO_2}}{l}$. The common unit of the permeability is Barrer, 1 Barrer = 10⁻¹⁰ cm³(STP)·cm/(s·cm²·cmHg). The common unit of the permeance is the gas permeation unit (GPU), 1 GPU = 10⁻⁶ cm³(STP)/(s·cm²·cmHg). The selectivity of CO₂/N₂, α_{CO_2/N_2} , is defined as the permeability ratio between CO₂ and N₂ as shown in Eq. 2.

2.5. Characterization of zeolite Y and membrane properties

The X-ray diffraction (XRD) pattern of zeolite particles was collected with the Rigaku Geigerflex X-ray powder diffractometer (Rigaku MSC, The Woodlands, TX) using CuKα

($\lambda=1.5405 \text{ \AA}$) radiation. The particle size of synthesized zeolite Y was characterized by dynamic light scattering (DLS) using Zetasizer Nano ZS (Malvern Instruments Inc., Westborough, MA).

The surface hydrophilicity of the bare PES300 substrate and the zeolite Y/PES300 support was evaluated by contact angle measurements using the sessile drop technique with deionized water as the reference liquid. About 1 μL deionized water droplet was deposited onto the leveled membrane surface to measure the contact angle of each sample.

The cross-section and surface morphology of the synthesized membranes were observed by scanning electron microscope (SEM) using FEI Nova NanoSEM400 (FEI Company, Hillsboro, OR).

3. Results and discussion

3.1. Zeolite Y synthesis

As is shown in Fig. 5, the XRD pattern of the synthesized zeolite sample matched the reference of zeolite Y very well, indicating that zeolite Y has been successfully synthesized. The particle size of synthesized zeolite Y was measured using DLS. As shown in Fig. 6, the average diameter of the synthesized zeolite Y was around 40 nm.

Fig. 5. XRD spectra of the synthesized zeolite Y and reference spectra of zeolite Y.

Fig. 6. Size distribution of the synthesized zeolite Y particles from DLS.

3.2. Membrane morphology via SEM

The SEM image in Fig. 7 shows the cross-section of the composite membrane synthesized in this work. As shown in this figure, the composite membrane with three layers was successfully synthesized. The three layers on top of the porous PES substrate were the nano zeolite Y layer, selective Pebax[®] layer and PDMS cover layer, from bottom to top. Zeolite Y particles were observed to be packed closely on top of the PES substrate, forming a much smaller pore size compared to the porous PES substrate. The thickness of the zeolite Y layer was around 300 nm. On top of the zeolite Y layer, the dense Pebax[®] layer showed a thickness of around 400 nm. The top-most layer of the composite membrane was the PDMS cover layer, which showed a thickness of around 100 nm. Such a composite membrane showed a CO₂ permeance of 940 GPU and a CO₂/N₂ selectivity of 30 at 57°C from the transport performance measurement.

Fig. 7. SEM image of the cross-section morphology of the composite membrane: (A) zeolite Y layer, (B) Pebax[®] layer and (C) PDMS cover layer.

3.3. Effect of Pebax[®] blend composition on membrane separation performance

To improve the performance of Pebax[®] membranes, Yave et al. incorporated different EO-containing small molecules including PEG200 and PEG-DME500 into the Pebax[®] solution [9,10,20]. With up to 50 wt.% of PEG200 or PEG-DME500 in the composition, a much higher permeability was obtained compared to the pure Pebax[®] membrane. The CO₂ permeability for a 50/50 ratio of Pebax[®]/PEG-DME500 membrane was reported to be around 850 Barrers, with a CO₂/N₂ selectivity of 30 at 50°C.

In this work, both PEG200 and PEG-DME500 were used as the EO-containing small molecules for blending into the Pebax[®] solution. It was found that higher CO₂ permeance could be obtained with increasing the amount of EO-containing small molecules in the membrane composition. However, when the PEG200 or PEG-DME500 content was too high, there was a significant reduction on the CO₂/N₂ selectivity of the membrane. This could be due to the fact that the polymer blend matrix was not stable with such a high content of small molecules. The maximum content of EO-containing small molecules in the blend solution was found to be 50 wt.% for PEG200 and 75 wt.% for PEG-DME500. Beyond these two values, the membranes showed a poor selectivity even with a PDMS cover layer due to the weak polymer blend matrix. It could be clearly shown in Table 1 that by incorporating PEG200 or PEG-DME500, the CO₂ permeance was much higher compared to the pure Pebax[®] membrane. This could be explained by two reasons. First, PEG200 or PEG-DME500 introduced more polar EO groups, which could enhance the solubility of CO₂ molecules into the membrane. Second, small molecules introduced more free volume and improved the flexibility of the polymer chains, which further enhanced the diffusivity of CO₂ molecules through the membrane. Based on the solution-

diffusion mechanism, higher CO₂ permeance could be obtained with both larger solubility and diffusivity.

Table 1. Composite membrane performances with different Pebax[®] layer compositions.

Sample No.	Selective layer composition*	CO ₂ permeance (GPU)	CO ₂ /N ₂ selectivity
1	Pebax [®]	342	32
2	Pebax [®] /PEG200 50/50 ¹	795	35
3	Pebax [®] /PEG-DME500 50/50 ²	839	31
4	Pebax [®] /PEG-DME500 25/75	940	30

*Pebax[®] layer coating conditions: 2 wt.% solution and 3000 rpm spinning speed.

¹Membranes prepared with the same composition showed a selectivity error bar of ± 2 .

²Membranes prepared with the same composition showed a selectivity error bar of ± 1.5 .

Another comparison could be made between PEG200 and PEG-DME500. From Table 1 (Samples 2 and 3), it could be seen that with the same amount (50 wt.%) of small molecules, the membrane with PEG200 showed a slightly higher CO₂/N₂ selectivity, while the membrane with PEG-DME500 showed a higher CO₂ permeance. This could be explained by the different structures of PEG200 and PEG-DME500. It can be seen from Fig. 2 that the PEG-DME500 molecule has two methyl end groups, which could introduce more free volume compared to PEG200 and further improve the CO₂ permeance. On the other hand, there were more EO groups in the Pebax[®]/PEG200 blend due to the lower molecular weight of PEG200, which provided more affinity to CO₂ molecules, resulting in a slightly higher CO₂/N₂ selectivity.

3.4. Influence of the zeolite Y layer on membrane separation performance

From our transport measurements, the CO₂/N₂ selectivity of zeolite Y layer on top of PES substrate was ~ 0.85 (close to Knudsen diffusion), which means that the zeolite Y layer itself did not contribute to the overall CO₂/N₂ selectivity of the membrane. This was mainly due to the fact that the zeolite Y layer was a porous layer, i.e., not a defect-free nonporous layer, and its main role was to serve as a substrate instead of a selective layer. However, the zeolite Y layer played a great role in improving the adhesion to the Pebax[®] layer and minimizing the defects.

The key to prepare a selective Pebax[®] layer with a high CO₂ permeance is to make it as thin as possible, due to the fact that the permeance is inversely proportional to the selective layer thickness. However, if the membrane is too thin, there will be defects in the selective layer, which could dramatically reduce the CO₂/N₂ selectivity. In this study, the zeolite Y layer played a big role to allow for the preparation of much thinner membranes due to its good adhesion with the Pebax[®] layer. Table 2 (Samples 2, 5, 4 and 6) and Fig. 8 show the comparison of the membrane separation performance with and without the zeolite Y layer. It could be seen that for thin (~ 400 nm) Pebax[®] layers, membranes without the zeolite Y layer showed a much lower CO₂/N₂ selectivity, indicating that there were defects in the membrane which could not be covered even with a PDMS cover layer. However, with the help of the zeolite Y layer, the membrane showed a relatively good CO₂/N₂ selectivity. This could be due to the fact that the zeolite Y layer was more hydrophilic than the PES substrate, which improved the adhesion with the Pebax[®] layer.

Since the solvent for the Pebax[®] solution was a hydrophilic ethanol/water mixture, it can be deduced that higher hydrophilicity of the substrate would help to improve the adhesion to the Pebax[®] solution. Without the zeolite Y layer, after coating, the solution could not cover all the surface of the PES substrate. At some places on top of the substrate, the solution aggregated and

caused defects on top, which led to a low CO₂/N₂ selectivity. With the zeolite Y layer, the solution was observed to cover all over the surface of the substrate, which helped to maintain a good CO₂/N₂ selectivity of the membrane. This could be further proved by the contact angle measurements of the bare PES substrate and the zeolite Y/PES substrate. The contact angle of a water droplet on bare PES substrate was measured to be around 30°, while with a zeolite Y layer, it reduced to only 3° (Fig. 8). The much lower contact angle indicated a higher hydrophilicity with the help of the zeolite Y layer, which could further improve the adhesion between the Pebax[®] layer and the substrate.

Table 2. Comparison of performances of composite membranes with and without the zeolite Y layer.

Sample No.	Pebax [®] layer composition	Zeolite Y layer (w/o)	CO ₂ permeance (GPU)	CO ₂ /N ₂ selectivity
2	Pebax [®] /PEG200 50/50 ¹	w	795	35
5	Pebax [®] /PEG200 50/50 ¹	o	1420	10
4	Pebax [®] /PEG-DME500 25/75 ¹	w	940	30
6	Pebax [®] /PEG-DME500 25/75 ¹	o	1615	8
7	Pebax [®] /PEG200 50/50 ²	w	610	38
8	Pebax [®] /PEG200 50/50 ²	o	527	37
9	Pebax [®] /PEG-DME500 25/75 ²	w	754	30
10	Pebax [®] /PEG-DME500 25/75 ²	o	661	30

¹ Pebax[®] layer coating conditions: 2 wt.% solution and 3000 rpm; Pebax[®] layer thickness: ~ 400 nm.

² Pebax[®] layer coating conditions: 2.5 wt.% solution and 3000 rpm; Pebax[®] layer thickness: ~ 500 nm.

Fig. 8. Comparison of CO₂/N₂ selectivities and substrate contact angles with and without the zeolite Y layer (Pebax[®] layer thickness: ~ 400 nm; compositions: Pebax[®]/PEG200 50/50 or Pebax[®]/PEG-DME500 25/75 and coating conditions: 2 wt.% solution and 3000 rpm spinning speed).

Thicker and defect-free composite membranes were also prepared to compare the transport performances with and without the zeolite Y layer. Table 2 (Samples 7 to 10) and Fig. 9 show that the composite membranes with the zeolite Y layer exhibited a higher CO₂ permeance compared to the membranes without the zeolite Y layer. This could be explained by the fact that

the zeolite Y layer had a smaller interparticle pore size than the PES substrate, which reduced the penetration of the Pebax[®] solution into the pores underneath. Therefore, the mass transfer resistance was further reduced, leading to a higher CO₂ permeance. Fig. 10 shows the surface morphology of the bare PES substrate (a) and the zeolite Y layer/PES substrate (b). According to the image analysis, the average pore size of the porous PES substrate was 72 nm, while the zeolite Y layer had an interparticle pore size of only around 10 nm. The smaller pore size was the key to reduce the penetration, therefore a higher CO₂ permeance was observed from the membranes with the zeolite Y layer.

Fig. 9. Comparison of membrane performances with and without the zeolite Y layer (Pebax[®] layer thickness: ~ 500 nm; compositions: Pebax[®]/PEG200 50/50 or Pebax[®]/PEG-DME500 25/75 and coating conditions: 2.5 wt.% solution and 3000 rpm spinning speed).

Fig. 10. SEM images of the surface morphology of (a) bare PES substrate and (b) zeolite Y layer/PES substrate.

3.5. Influence of PDMS cover layer on membrane performance

Even though the zeolite Y layer can improve the adhesion between the Pebax[®] layer and the substrate, there will still be some defects existing on the Pebax[®] layer if it is too thin. To prevent the pin-hole defects in the thin polymer layer, a PDMS cover layer was applied on top of the composite membrane. PDMS is a low-cost polymer with good flexibility, non-toxicity and good resistance to heat or moisture. Besides, it is among the most gas permeable materials available for use as the caulking layer [31]. According to literature, PDMS has a CO₂ permeability of 3800 Barrers at 35°C [32]. All of these advantages make PDMS a good choice to develop a protective coating layer on top of membranes. In this work, the PDMS solution was spin-coated on top of the selective Pebax[®] layer to make a thin layer with a thickness of around 100 nm. The CO₂/N₂ selectivity of the PDMS cover layer from our transport measurement was around 3.5 – 4.5, which was much lower than the Pebax[®] layer itself (~ 30). This indicated that the Pebax[®]

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4 layer was the major selective layer for the composite membrane. The PDMS layer contributed a
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6 little to the overall selectivity, but the major role of the PDMS layer was used for the caulking
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8 purpose to cover the defects in the Pebax[®] layer.
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11 Fig. 11 shows the transport performances of composite membranes with and without the
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13 PDMS cover layer. All the membrane preparation conditions for the Pebax[®] layer were the same
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15 (2 wt.% solution and 3000 rpm spinning speed). It could be clearly seen that without the PDMS
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17 layer, the CO₂/N₂ selectivities of the membranes were dramatically lower, which indicated that
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Fig. 11. Comparison of membrane performances with and without the PDMS cover layer (Pebax[®] layer compositions: Pebax[®]/PEG200 50/50 or Pebax[®]/PEG-DME500 25/75 and coating conditions: 2 wt.% solution and 3000 rpm spinning speed).

3.6. Effects of Pebax[®] layer coating conditions on membrane separation performance

In this study, different membrane preparation conditions for the Pebax[®] layer including the spinning speed and the Pebax[®] blend solution concentration were investigated. These two factors played a big role on controlling the thickness of the selective Pebax[®] layer. Basically, a higher spinning speed or lower casting solution concentration will lead to a thinner selective layer, which provides a higher CO₂ permeance. However, if the membrane is too thin, the membrane will leak due to defects, which will lead to a very low CO₂/N₂ selectivity.

From Fig. 12, it could be seen that the composite membrane with a Pebax[®]/PEG-DME500 layer showed a higher CO₂ permeance with a higher spinning speed. However, when the

spinning speed was higher than 3000 rpm, there was an obvious decline on the CO₂/N₂ selectivity. This meant that the membrane was too thin and no longer defect-free. Even with a PDMS cover layer, those defects could not be covered completely. The composite membrane with a Pebax[®]/PEG200 layer showed a similar trend (Fig. 13).

Fig. 12. Effects of Pebax[®] layer spinning speed on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (Pebax[®] layer composition: Pebax[®]/PEG-DME500 25/75; total solid concentration: 2 wt.%).

Fig. 13. Effects of Pebax[®] layer spinning speed on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (Pebax[®] layer composition: Pebax[®]/PEG200 50/50; total solid concentration: 2 wt.%).

Similarly, it was indicated from Fig. 14 and Fig. 15 for Pebax[®]/PEG-DME500 25/75 and Pebax[®]/PEG200 50/50 membranes, respectively, the CO₂ permeance increased with a lower total solid concentration of the casting solution due to a thinner membrane thickness. However, when the solution concentration was below 2 wt.%, the CO₂/N₂ selectivity decreased dramatically, indicating that there were too many defects in the selective Pebax[®] layer which could not be covered by the PDMS layer.

Fig. 14. Effects of Pebax®/PEG-DME500 (25/75) blend solution concentration on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (spinning speed: 3000 rpm).

Fig. 15. Effects of Pebax[®]/PEG200 (50/50) blend solution concentration on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (spinning speed: 3000 rpm).

3.7. Effect of water vapor on membrane separation performance

Researchers have done some investigations regarding the water vapor effect on the Pebax membrane separation performance. Lokhandwala and Baker [33] showed that the CO₂ flux was reduced by 40 – 45 % with the presence of water vapor for natural gas treatment. However, an encouraging study done by Reijerkerk [34] showed that the CO₂ permeability only dropped by 5 – 10 % at 50°C with a H₂O/CO₂/N₂ ternary mixed gas compared to the dry CO₂/N₂ binary mixed gas. This indicates that at the low feed pressures (and thus low partial pressures of CO₂) in flue gas, the CO₂ transport performance would not be affected too much by water.

In this work, the effect of water vapor on membrane separation performance was also investigated. Table 3 shows the comparison of membrane performances with and without water

vapor. The same piece of the membrane was tested under both dry and wet conditions. It was indicated that with 17 % water vapor, the CO₂ permeance dropped by only 5 %. This was different from the behavior generally observed for PEO-containing polymers at high CO₂ partial pressures such as for the natural gas. Since the Pebax membrane in this work was mainly for CO₂ separation from flue gas, which was operated at a low CO₂ partial pressure, the CO₂ transport was not reduced a lot by water vapor.

Table 3. Comparison of performances of composite membranes with and without water vapor¹.

Sample No.	Testing condition (dry/wet)	Water content in both the feed and sweep gas	CO ₂ permeance (GPU)	CO ₂ /N ₂ selectivity
11	dry	0 %	912	29
11	wet	17 %	867	30

¹ Pebax[®] layer composition: Pebax[®]/PEG-DME500 25/75; Pebax[®] layer coating conditions: 2 wt.% solution and 3000 rpm.

3.8. Stability of Pebax[®]/zeolite Y composite membrane

Fig. 16 shows the 24 h stability test of the Pebax[®]/zeolite Y composite membrane with an average CO₂ permeance of 940 GPU and a CO₂/N₂ selectivity of 30. It could be seen that the membrane performance was stable within 24 h. No sign of dropping was observed for either CO₂ permeance or CO₂/N₂ selectivity. Regarding the fact that there was no component in the composite membrane which is sensitive to SO₂, it could be deducted that the Pebax[®]/zeolite Y composite membrane would be suitable for the application of CO₂ separation and capture from flue gas [35].

Fig. 16. Membrane performance during the 24 h stability test at 57°C (Pebax[®] layer composition: Pebax[®]/PEG-DME500 25/75 and coating conditions: 2 wt.% solution and 3000 rpm spinning speed).

4. Conclusions

A new Pebax[®] 1657/ zeolite Y composite membrane was successfully synthesized. With the help of a nano zeolite Y layer on top of the PES substrate, the adhesion between the Pebax[®] 1657 layer and the substrate was improved, which was confirmed by the fact that the contact angle of the substrate reduced from 30° (bare PES) to 3° (zeolite Y layer/PES). This better adhesion could allow for the preparation of much thinner membranes, which provided a higher CO₂ permeance while maintaining a good CO₂/N₂ selectivity. Moreover, the zeolite Y layer showed a

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4 smaller interparticle pore size (~ 10 nm) compared to the pore size of the bare PES substrate (~
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6 72 nm). This smaller pore size reduced the penetration of the Pebax[®] 1657 solution into the
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8 pores underneath, which could further reduce the mass transfer resistance, leading to a higher
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10 CO₂ permeance. PDMS was proved to be effective for covering the defects of the thin Pebax[®]
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12 1657 layer, which could help maintaining a good CO₂/N₂ selectivity of the composite membrane.
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17 The membrane preparation conditions such as the spinning speed of the spin-coating,
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19 solution concentration and composition of the Pebax[®] 1657 blend with EO-containing small
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21 molecules, were also studied and optimized. Finally, the resulting composite membrane showed
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23 a CO₂ permeance of 940 GPU and a CO₂/N₂ selectivity of 30 at 57°C, which was stable for 24 h.
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25 Compared to most of work done on Pebax[®] membranes so far, this work for the first time reports
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27 a thin Pebax[®] membrane (less than 500 nm) with a high CO₂ permeance of 940 GPU and a
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29 relatively good CO₂/N₂ selectivity of about 30.
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Nomenclature

J gas flux

J_{CO_2} flux of CO_2

l membrane thickness

P permeability

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

$p_{f_{CO_2}}$ CO_2 partial pressure on the feed side of the membrane

$p_{p_{CO_2}}$ CO_2 partial pressure on the permeate side of the membrane

Greek letters

α selectivity

α_{CO_2/N_2} selectivity of CO_2 over N_2

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Figures

Fig. 1. Schematics of CO₂/N₂ transport mechanisms through polymer and inorganic membranes.

Pebax[®] 1657
Weight ratio of PA6/PEO: 40/60

PEG

PEG-DME

Fig. 2. Chemical structures of Pebax[®] 1657, PEG and PEG-DME.

Fig. 3. Schematic of Pebax[®]/zeolite Y composite membrane structure.

Fig. 4. Schematic of the preparation procedure of the Pebax[®]/zeolite Y composite membrane.

Fig. 5. XRD spectra of the synthesized zeolite Y and reference spectra of zeolite Y.

Fig. 6. Size distribution of the synthesized zeolite Y particles from DLS.

Fig. 7. SEM image of the cross-section morphology of the composite membrane: (A) zeolite Y layer, (B) Pebax[®] layer and (C) PDMS cover layer.

Fig. 8. Comparison of CO₂/N₂ selectivities and substrate contact angles with and without the zeolite Y layer (Pebax[®] layer thickness: ~ 400 nm; compositions: Pebax[®]/PEG200 50/50 or Pebax[®]/PEG-DME500 25/75 and coating conditions: 2 wt.% solution and 3000 rpm spinning speed).

Fig. 9. Comparison of membrane performances with and without the zeolite Y layer (Pebax® layer thickness: ~ 500 nm; compositions: Pebax®/PEG200 50/50 or Pebax®/PEG-DME500 25/75 and coating conditions: 2.5 wt.% solution and 3000 rpm spinning speed).

Fig. 10. SEM images of the surface morphology of (a) bare PES substrate and (b) zeolite Y layer/PES substrate.

Fig. 11. Comparison of membrane performances with and without the PDMS cover layer (Pebax® layer compositions: Pebax®/PEG200 50/50 or Pebax®/PEG-DME500 25/75 and coating conditions: 2 wt.% solution and 3000 rpm spinning speed).

Fig. 12. Effects of Pebax[®] layer spinning speed on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (Pebax[®] layer composition: Pebax[®]/PEG-DME500 25/75; total solid concentration: 2 wt.%).

Fig. 13. Effects of Pebax[®] layer spinning speed on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (Pebax[®] layer composition: Pebax[®]/PEG200 50/50; total solid concentration: 2 wt.%).

Fig. 14. Effects of Pebax[®]/PEG-DME500 (25/75) blend solution concentration on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (spinning speed: 3000 rpm).

Fig. 15. Effects of Pebax[®]/PEG200 (50/50) blend solution concentration on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (spinning speed: 3000 rpm).

Fig. 16. Membrane performance during the 24 h stability test at 57°C (Pebax[®] layer composition: Pebax[®]/PEG-DME500 25/75 and coating conditions: 2 wt.% solution and 3000 rpm spinning speed).