Multilayer polymer/zeolite Y composite membrane structure for CO₂ capture from flue gas

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Abstract

A novel concept of multilayer polymer/zeolite Y composite membrane structure was developed and investigated for CO₂ capture from flue gas. Zeolite Y nanoparticles with an average particle size of 40 nm were successfully deposited onto flexible polymer supports with uniform coverage by the vacuum-assisted dip deposition approach. The zeolite Y dispersion concentration was varied for different commercial polymer supports to obtain a crack-free zeolite Y layer. Scanning electron microscopy (SEM) analysis indicated that a uniform zeolite Y layer could be formed either on Biomax polyethersulfone (PES) membrane or on TM10 polyvinylidene fluoride (PVDF) membrane with appropriate vacuum-assisted dip deposition conditions. Atomic force microscopy (AFM) analysis showed that the zeolite Y/Biomax PES substrate was smoother than the zeolite Y/TM10 PVDF substrate. The Pebax[®]/PEG-200 membrane prepared on the zeolite Y/Biomax PES substrate exhibited higher CO₂ permeance than that prepared on the bare Biomax PES support since the penetration of the polymer membrane was minimized by the smaller interparticle pore size on the zeolite Y layer. The membrane of the multilayer composite structure showed a CO₂ permeance of 745 GPU and a CO₂/N₂ selectivity of 25.4 under flue gas operating conditions at 57°C and ~1 atm. This concept has provided the basis for high performance membranes with the selective polymer cover layer containing amino groups and for grown zeolite Y membranes with continuous polycrystalline structure supported by the flexible polymer substrate.

Keywords: CO₂ capture; Flue gas; Zeolite Y nanoparticle; Polymer support; Multilayer composite membrane

1. Introduction

Membrane separation is one of the most effective technologies for CO₂ capture from flue gas to reduce its emission into the atmosphere as a major greenhouse gas. Therefore, intensive research work has been done to develop novel membrane materials to improve gas separation performances. Porous inorganic membranes typically consist of a thin selective inorganic layer on the top for gas separation and a thick macroporous inorganic layer at the bottom for mechanical stability [1-3], which can provide a good selectivity with a reasonably high permeance [1,4]. However, the membrane performance is difficult to reproduce due to the defects introduced during fabrication and/or handling. In addition, the inorganic supports are fragile, expensive, and hard to fabricate in large scale [5,6]. As a result, the poor reproducibility and high manufacture cost have hindered the commercialization of inorganic membranes for CO₂ capture. On the other hand, polymeric membranes can be fabricated continuously in large scale with inexpensive polymeric supports. Moreover, they are flexible and easily scaled up in the form of spiral-wound and hollow-fiber modules with a high surface/volume ratio and a small footprint, which are desired for the retrofit of existing coal-fired power plants. However, the separation performances of polymeric membranes based on the solution-diffusion mechanism suffer from the Robeson's upper bound [7], although some of them have demonstrated high CO₂ permeances [8,9].

In order to utilize the advantages from both inorganic and polymeric membranes, a novel concept of multilayer polymer/inorganic composite membrane has been developed for cost-effective post-combustion CO₂ capture from flue gas (Fig. 1) [10]. As described earlier, polymer support with low manufacture cost is preferred as the substrate for the deposition of inorganic particles. Therefore, ultrafiltration and microfiltration membranes synthesized via the phase

inversion technique are potential candidates for this purpose. These polymer supports are commercially available in polyethersulfone (PES), polysulfone (PSF), polyvinylidene fluoride (PVDF), polyacrylonitrile, etc.

As microporous crystalline aluminosilicates, zeolites have well-defined pore sizes at Angstrom level [11-13]. Window structures, such as 12-membered ring, 10-membered ring, and 8-membered ring, determine the pore size in different zeolite frameworks. Based on their specific pore sizes, zeolites are considered as molecular sieves to differentiate between molecules of different sizes and shapes for separation purposes. In addition, the Si/Al ratio and the neutralizing cations can be modified to change the adsorption properties of zeolites (e.g., increase Si/Al ratio to obtain greater hydrophobicity) [14,15]. For CO₂ capture from flue gas, the effective separation of CO₂ from N₂ with high selectivity is hard to achieve based on pure molecular sieving mechanism, because their kinetic molecular sizes are very similar (CO₂ 3.3 Å vs. N₂ 3.6 Å) [7]. Moreover, the diffusion of gas molecules through the small pores having molecular sieving effects could be slow due to the steric hindrance, resulting in a low permeance [14]. On the other hand, the quadrupole moment and the polarizability of the CO₂ molecule are roughly three times and two times of those of the N₂ molecule, respectively [16]. In this case, separation will take place if the porous inorganic material could preferentially adsorb CO₂ molecules on its surface over N₂ molecules, even though its pore size is too large to have molecular sieving effects. Therefore, zeolites with relatively large pore size and tunable adsorption properties are considered as potential inorganic materials for CO₂/N₂ separation.

In view of its crystalline structure containing a three-dimensional lattice of “super-cages” connected by the “windows” (12-membered ring) of 7.4 Å (Fig. 2), zeolite Y is one of the promising zeolite materials for CO₂ capture from flue gas. First of all, its pore size is large

enough to avoid steric hindrance for gas diffusion. Secondly, CO₂ molecules tend to occupy the surface of zeolite Y pores due to the preferential interactions (e.g., polar-polar affinity) with zeolite Y framework and non-framework cations, resulting in a decreased window aperture size to reduce or even block the transport of N₂ molecules. Then, the adsorbed CO₂ molecules can diffuse along the concentration gradient on the surface through the pore by the surface-diffusion mechanism. It has been predicted by molecular dynamic simulation that the zeolite Y crystalline structure (Fig. 2) can obtain a CO₂ permeability of greater than 10⁵ Barrers (1 Barrer = 10⁻¹⁰ cm³ (STP)·cm/(cm²·s·cmHg)) with a CO₂/N₂ selectivity of higher than 200 under flue gas separation conditions [14], which well exceeds Robeson's upper bound for polymer membranes.

In order to obtain the inherent good selectivity from zeolite Y pores, zeolite crystals need to be interconnected with each other to form a continuous polycrystalline structure. Secondary growth is one typical approach to prepare zeolite membranes [17-23]. This method involves the deposition of a zeolite seed (small zeolite particle) layer on a solid inorganic support and the following densification of the zeolite membrane in the secondary growth process [24]. White et al. [2] reported a CO₂ permeance of 300 GPU (1 GPU = 10⁻⁶ cm³ (STP)/(cm²·s·cmHg)) and a CO₂/N₂ selectivity of more than 500 with a zeolite Y membrane on alumina support via this secondary growth approach. Kuzniatsova et al. [13] indicated that the quality of the deposited zeolite seed layer had significant effects on the quality of grown zeolite membrane. Other researchers reported that the cracks or defects in the zeolite seed layer could result in a defective zeolite membrane [24,25]. Therefore, one important part of this research work was to identify a suitable polymer support and optimize the processing conditions to deposit a thin defect- and crack-free zeolite Y seed layer with uniform coverage. This is not only imperative for the aforementioned secondary growth of zeolite Y membrane, but also essential for the coating of a

selective polymer cover layer (Fig. 1), which was investigated and will be discussed later in this study.

Spin coating [26,27], rubbing [19,28], and dip coating [2,13,29,30] are the common deposition methods reported in the literature. The spin coating approach was only suitable for the deposition of particles onto the support with similar hydrophilicity [26], and it is not applicable in large-scale fabrication. The rubbing approach is capable of depositing particles onto the support with different hydrophilicities. However, it is hard to obtain uniform particle layers, and the procedure is difficult to be standardized for large-scale synthesis [19]. Compared to these two approaches, dip coating is more promising for practical application due to its good scale-up capability, simple instrumentation, and few requirements of particle/support pre-treatment.

In this study, a vacuum-assisted dip deposition approach was developed and applied for the deposition of zeolite Y nanoparticles on polymer supports (Fig. 3). Three kinds of commercial microfiltration/ultrafiltration polymer membranes, Biomax[®] PES membrane with molecular weight cut off (MWCO) of 300 kilo-Daltons (kDa) from EMD Millipore Corporation, TM10 PVDF membrane from TriSep Corporation, and NL PSF membrane from NL Chemical Technology, Inc., were investigated for their suitability of serving as the supporting material for zeolite Y deposition. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to determine the suitable polymer supports and optimize the deposition conditions. At the end, a selective polymer cover layer consisting of Pebax[®] 1657 and polyethylene glycol (average $M_w = 200$) blend was applied on top of the zeolite/polymer substrate by spin coating for CO₂/N₂ separation. The Pebax[®] 1657/polyethylene glycol ratio was varied to study their effects on membrane separation performance under flue gas operating

conditions (dry feed gas containing 20% CO₂ and 80% N₂) at 57°C and about 1 atm. The same membranes were also prepared on the bare polymer support for comparison to investigate the effects of the zeolite/polymer substrate.

2. Experimental

2.1. Materials

Zeolite Y nanoparticles with an average size of 40 nm after their synthesis were used directly without removing water from the zeolite Y pores by incineration. The Biomax[®] polyethersulfone ultrafiltration membrane with MWCO of 300 kDa (Biomax PES) was purchased from EMD Millipore Corporation (Billerica, MA). This support was first soaked in deionized water overnight and then in isopropanol (IPA) to remove the glycerol inside its pores. The TM10 polyvinylidene fluoride membrane (TM10 PVDF) was kindly supplied by TriSep Corporation (Goleta, CA). The NL polysulfone membrane (NL PSF) was kindly provided by NL Chemical Technology, Inc. (Mount Prospect, IL). These two supports were used as received. Polyethylene glycol (PEG-200, average M_w = 200), ethanol (99.5%+), and heptane (anhydrous, 99%) were purchased from Sigma-Aldrich (Milwaukee, WI). Isopropanol (IPA, 99.9%) was acquired from Fisher Scientific Inc. (Pittsburgh, PA). Pebax[®] 1657 (Pebax[®]) was kindly donated by Arkema Inc. (Philadelphia, PA).

2.2. Membrane preparation

2.2.1. Zeolite Y deposition

The deposition of zeolite Y nanoparticles onto the polymer support was achieved by a vacuum-assisted dip deposition apparatus (Fig. 3). The polymer support was taped onto a macroporous sintered plate (average pore size of ~ 100 μm) which was supported by a plastic

holder with channels. The combination of the plastic holder and the sintered plate was employed to achieve a uniform distribution of vacuum suction throughout the polymer support, which was important to obtain a uniform deposition rate of zeolite Y nanoparticles. Zeolite Y nanoparticles were dispersed in deionized water with different concentrations under a pre-determined pH by ultrasonication. The surface of the polymer support was dipped tangentially into the zeolite Y dispersion for 4 seconds when the vacuum was turned on. A bypass consisting of a needle valve and a vacuum gauge was installed to control and monitor the vacuum degree during the deposition process. The vacuum degree was maintained as 3 in Hg for all the deposition experiments in this study. After deposition, the zeolite Y/polymer substrates were dried overnight at ambient conditions before characterization or coating with selective polymer cover layer for gas transport measurements.

2.2.2. Selective polymer cover layer preparation

Pebax[®] was dissolved in a water/ethanol (30/70 weight ratio) mixture at 80°C overnight under reflux and magnetic stirring to obtain a homogeneous solution with 2 wt% Pebax[®] concentration. This solution was then cooled down to room temperature. Different amounts of PEG-200 and water/ethanol solvent were added into the Pebax[®] solution under stirring for at least 1 hour to achieve a homogeneous and transparent Pebax[®]/PEG-200 solution. The Pebax[®]/PEG-200 solution was applied onto the polymer or zeolite Y/polymer substrate by using the WS-650 spin coater (Laurell Technologies Corporation, North Wales, PA). The substrate was first filled with heptane to prevent possible penetration of the dilute coating solution. After heptane disappeared from the substrate surface, the Pebax[®]/PEG-200 solution was spread uniformly on the substrate before starting the spin coating procedure. The spinning speed was increased to 1000 rpm and maintained for 10 seconds. Then, it was further increased to 3000

rpm and kept for one minute. After spin coating, the membranes were dried under ambient conditions for at least 4 hours before gas transport measurements. This operating procedure was kept the same for all the experiments.

2.3. Membrane morphology characterization

Optical microscopy (Nikon Epiphot, Melville, NY) was used to estimate the coverage of zeolite Y nanoparticles on the polymer support in relatively large scale. In order to confirm the coverage of zeolite Y on the polymer support and determine the thicknesses of different layers, scanning electron microscopy (SEM) was employed to analyze the sample surface and cross section morphology. SEM images were taken by a Nova 400 NanoSEM (FEI Company, Hillsboro, OR) and some of the images were analyzed by using Clemex Vision Professional Edition (Longueuil, Quebec, Canada) software to determine the pore size and porosity of different polymer supports. Atomic force microscopy (AFM) was applied to analyze the surface roughness of the polymer supports with and without zeolite Y deposition. AFM images were taken by a Nanoscope V scanning probe microscope (Bruker Inc., Billerica, MA) and analyzed by using NanoScope Analysis (Veeco Instruments Inc., Plainview, NY) software.

2.4. Gas transport measurements

The gas transport measurements were performed by using a gas permeation apparatus shown in Fig. 4. A rectangular stainless steel cell with an effective membrane area of 3.4 cm^2 was employed for conducting the gas separation measurement to evaluate membrane performance. The feed gas and sweep gas flows were countercurrent. This permeation cell was enclosed in an oven (BEMCO Inc., Simi Valley, CA) for the accurate temperature control at 57°C . The feed gas and sweep gas flow rates were precisely controlled and maintained at 60 and $30 \text{ cm}^3/\text{min}$ by Brooks flow-meters (Brooks Instrument, Hatfield, PA), respectively. The feed gas composition

was 20% CO₂ and 80% N₂ (dry gas). Argon was used as the sweep gas for the simplicity of gas chromatography (GC) analysis. The retentate pressure was controlled by a back-pressure regulator at 1.6 psig (measured by a pressure gauge), and the permeate pressure was set at 1.2 psig (measured by another pressure gauge). Table 1 summarizes the test conditions for the gas permeation experiments.

After the gas transport in the permeation cell, the retentate and permeate gas samples were injected into an Agilent 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA) with SUPELCO Carboxen[®] 1004 micro-packed column (Sigma-Aldrich, St. Louis, MO) for gas composition analysis. After the desired operating conditions (temperature, pressure, and flow rates) were achieved, each membrane sample was tested for at least 5 hours to obtain the representative results at the steady state.

The gas separation performance of the membrane was characterized by two parameters: selectivity and permeance [31]. The selectivity, also known as the separation factor, is defined as:

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j} \quad (5.1)$$

The permeance of a particular gas is defined as:

$$P_i = \frac{P_{e,i}}{l} = \frac{J_i}{\Delta p_i} \quad (5.2)$$

The common unit of P_i is GPU which is 10⁻⁶ cm³ (STP)/(cm²·s·cmHg) and that of $P_{e,i}$ (permeability) is Barrer which is 10⁻¹⁰ cm³ (STP)·cm/(cm²·s·cmHg). The CO₂/N₂ selectivity and CO₂ permeance were calculated for each membrane sample based on the GC analyses obtained at the steady state for membrane performance evaluation.

3. Results and discussion

3.1. Biomax PES support for zeolite Y deposition

During the vacuum-assisted dip coating process, the liquid (water) of the zeolite Y dispersion flowed through the polymer support due to the pressure differential created by the vacuum from the back of the polymer support. Depending on the pore size of the polymer support, zeolite Y nanoparticles (40 nm particle size) could be retained on the support surface to form a layer, while the water could pass through the porous polymer support. Therefore, the concentration of zeolite Y in the dispersion has significant effects on the formation of a thin zeolite Y layer with full coverage on the polymer support. The pH of zeolite Y dispersion was kept as 7 for the experiments performed in this work.

Fig. 5 shows the surface morphology of the Biomax PES support under different magnifications. As shown in Table 2, the image analysis indicated that its average pore size was 72.0 nm and its surface porosity was 15.8%. Although this average pore size was larger than the average particle size of zeolite Y, the tortuosity of the porous PES layer could prevent zeolite Y nanoparticles from traveling to the other side of the support. As shown in Fig. 6(a), (b), and (c), multiple times of depositing 0.001 wt% zeolite Y dispersion were required for increasing the amount of zeolite Y nanoparticles deposited onto the support for better coverage. On the other hand, one time of depositing 0.01 wt% zeolite Y dispersion resulted in most particles staying on the support surface between the pores (Fig. 7(a)), whereas ten times of depositing 0.001 wt% zeolite Y dispersion allowed the majority of particles to fill the pores (Fig. 6(c)). Theoretically, the amounts of zeolite Y nanoparticles deposited onto the support could be identical in both cases. However, since the pore size of the support was larger than the particle size of zeolite Y, the first time of depositing 0.001 wt% dispersion resulted in some nanoparticles deposited inside

the pores. This could reduce the effective pore size and retain more nanoparticles during the next deposition process. Moreover, in the second deposition process, the zeolite Y dispersion preferred to flow through the larger pores due to the lower resistance, which could improve the uniformity of this pore-filling effect. As a result, both the amount and the size of the pores on the support surface were significantly reduced after ten times of depositing 0.001 wt% dispersion. In comparison, all the zeolite Y nanoparticles went onto the support at once with less uniform distribution via one time of depositing 0.01 wt% dispersion, resulting in more and relatively larger pores remained on the surface.

However, the multiple-time deposition process might not be practical for real applications. Therefore, the concentration of zeolite Y dispersion was increased to deposit more nanoparticles on the support surface for better coverage with one-time deposition. As shown in Fig. 7(a), (b), and (c), the coverage of zeolite Y layer on the Biomax PES support was improved as the dispersion concentration increased from 0.01 wt% to 0.09 wt%. With 0.09 wt% zeolite Y dispersion, the nanoparticles filled all the pores on the support and formed a uniform and crack-free layer on top. However, when the dispersion concentration was further increased to 0.12 wt% (Fig. 7(d)), cracks could be observed on the sample surface, which could be attributed to the thicker zeolite Y layer bearing larger mechanical stresses [32]. The sample prepared with 0.09 wt% zeolite Y was evaluated by the optical microscopy, which showed a distinct colorful pattern on the surface (Fig. 8(b)) in comparison with the bare Biomax PES support (Fig. 8(a)). As a result, 0.09 wt% was determined to be the optimal concentration for the deposition of zeolite Y nanoparticles on the Biomax PES support.

3.2. TM10 PVDF support for zeolite Y deposition

The surface morphology of TM10 PVDF support under different magnifications is shown in Fig. 9. The image analysis revealed that it had an average pore size of 55.2 nm with a surface porosity of 11.5% (Table 2). The effects of zeolite Y dispersion concentration on the formation of a zeolite Y layer were investigated for this support. As shown in Fig. 10(a), the support surface was partially covered by the zeolite Y nanoparticles with one time of depositing the 0.07 wt% dispersion. When the concentration was increased to 0.09 wt%, a uniform zeolite Y layer was formed on the surface with complete coverage (Fig. 10(b)). Nevertheless, there were cracks on the zeolite Y layer when the concentration was further increased to 0.12 wt% (Fig. 10(c)). This phenomenon was similar to what was observed for the Biomax PES support, which resulted from more zeolite Y nanoparticles deposited onto the support.

The uniform zeolite Y layer on the TM10 PVDF support was expected to be obtained with a lower dispersion concentration than that for the Biomax PES support, because its pore size was smaller and more zeolite nanoparticles could be retained on the surface. However, the experimental results showed that the same dispersion concentration (0.09 wt%) was required to obtain good zeolite Y coverage on the TM10 PVDF support. This could be explained by the different surface morphologies and support materials. Both the pore size and porosity of the TM10 PVDF support were smaller than those of the Biomax PES support (Table 2), which increased the resistance to water transport through the membrane. In addition, PVDF is much more hydrophobic than PES. Therefore, the dispersion flux through this support was lower under the same vacuum-assisted dip deposition conditions, which resulted in a smaller total amount of zeolite Y nanoparticles deposited onto the support. As exhibited in Fig. 11, the sample deposited with 0.09 wt% dispersion showed a uniform colorful pattern on the surface due to the good coverage of zeolite Y nanoparticles.

3.3. *NL PSF support for zeolite Y deposition*

Since the pore size of NL PSF support was small, only the SEM image with large magnification was selected and shown in Fig. 12 to exhibit its surface morphology. The average pore size and porosity were determined as 12.1 nm and 5.3% by image analysis, respectively (Table 2). Different zeolite Y dispersion concentrations were employed to achieve good zeolite Y coverage on the NL PSF support. However, the suction of the dispersion through the membrane was not uniform and some liquid remained on the surface after the vacuum-assisted dip deposition process. This could be attributed to the small pore size/porosity and relatively hydrophobic PSF material, which significantly inhibited the water in the zeolite Y dispersion from flowing through the membrane even though a high degree of vacuum was applied on the back side. In this case, the increase of dispersion concentration could not improve the coverage of zeolite nanoparticles on the surface (Fig. 13). As a result, it could not form a uniform zeolite Y layer with complete coverage on the NL PSF support.

3.4. *Comparison between Biomax PES and TM10 PVDF supports for zeolite Y deposition*

In order to identify the best polymer supports for zeolite Y deposition, AFM analysis was performed to evaluate the surface roughness of the bare polymer supports and the polymer supports with the zeolite Y layer on top. As shown in Fig. 14, the average surface roughness of the Biomax PES support was reduced from 17 nm to 11 nm by the deposition of zeolite Y nanoparticles. Similarly, the average surface roughness of TM10 PVDF support was also decreased from 46 nm to 25 nm (Fig. 15). Table 3 summarizes the results of surface roughness measurements for these two supports with and without zeolite Y deposition for comparison. In both cases, the zeolite Y nanoparticles first filled in the “valleys” and then formed a continuous layer on the polymer surface during the vacuum-assisted dip deposition process, which resulted

in a smoother surface. The surface roughness of the substrate could affect the gas separation performance of the selective polymer cover layer on top, especially for thin membranes. The substrate with a smoother surface could allow a thinner polymer layer to be applied for complete coverage due to the smaller height difference between the “peak” and “valley” features. This is important for reducing the mass transfer resistance for high gas permeance while maintaining the good selectivity at the same time. Therefore, the zeolite Y/Biomax PES composite support was selected as the substrate for the application of the selective polymer cover layer in the next section. Fig. 16 indicates that a continuous zeolite Y layer was formed on the surface of the Biomax PES support with a thickness of around 500 nm.

3.5. Separation performance of multilayer zeolite Y/polymer composite membrane

The deposited zeolite Y layer obtained in the previous section consisted of individual nanoparticles (40 nm) with interparticle pores, which resulted in no CO₂/N₂ selectivity (see Section 3.5.2). The secondary zeolite Y growth on this zeolite Y/Biomax PES substrate to obtain a crack-free interconnected polycrystalline structure was still under investigation to achieve high CO₂/N₂ selectivity by zeolite Y itself. Therefore, a selective polymer cover layer was employed in this work to improve the selectivity of the multi-layer composite membrane and study the effects of the intermediate zeolite Y layer on membrane separation performance. Pebax[®] is the trade name for a family of commercial block copolymers consisting of two micro-separated phases: polyethylene oxide (PEO) phase and polyamide (PA) phase. The PEO segments contribute to high CO₂ permeability and selectivity due to their strong interactions with CO₂ molecules [33], while the crystalline PA segments provide good mechanical strength and film formation capability. These copolymers have demonstrated great potential for CO₂ separation from N₂ and H₂ [34-38]. Car et al. [39,40] prepared Pebax[®]/PEG membrane on polyacrylonitrile

(PAN) support by the dip coating and showed good CO₂ permeability. This concept was utilized to synthesize the multilayer zeolite Y/polymer composite membrane for CO₂ capture from flue gas. As shown in Fig. 17, the spaces between individual zeolite Y nanoparticles were covered by the Pebax[®]/PEG-200 layer to prevent the non-selective transport of CO₂/N₂ gas mixture through such regions.

3.5.1. Effects of PEG-200 content

The total solid concentration of the coating solution was maintained as 2 wt%, while different amounts of PEG-200 were blended with Pebax[®] to investigate the effect of PEG-200 content on the gas separation performance of the Pebax[®]/PEG-200 membrane prepared on the zeolite Y/Biomax PES substrate. As shown in Fig. 18, the CO₂ permeance was increased significantly from 102 GPU to 745 GPU by increasing the percentage of PEG-200 in the membrane composition. The incorporation of PEG-200 could increase the free volume of the dense Pebax[®] layer to reduce the mass transfer resistances for both CO₂ and N₂ molecules. Moreover, PEG-200 itself has great affinity to CO₂ molecules, which could perform the same function as the PEO segments in Pebax[®] to increase CO₂ solubility. Therefore, the CO₂/N₂ selectivity did not decrease much after the addition of PEG-200.

On the other hand, when the content of PEG-200 was increased from 50 wt% to 75 wt%, a further reduction of CO₂/N₂ selectivity from 27.4 to 25.4 was observed. The reason could be that the hard PA segments in Pebax[®] were insufficient to form a good membrane matrix in the presence of a large amount of small molecules (e.g., 75 wt% PEG-200). Fig. 19 exhibits the cross-section structure of this multi-layer inorganic/polymer composite membrane, which indicated that the thickness of the Pebax[®]/PEG-200 layer (50 wt% PEG-200) was about 350 nm and that of the zeolite Y layer was around 500 nm.

3.5.2. Effects of zeolite Y/Biomax PES substrate

As reported in the previous work from our group [41], the CO₂ permeance reduced from ~ 3670 GPU to ~ 3000 GPU at room temperature after the deposition of zeolite Y nanoparticles on the Biomax PES support, while the CO₂/N₂ selectivity was 1.2 in both cases. This indicated that the interparticle pores in the zeolite Y layer resulted in non-selective transport of CO₂/N₂ gas mixture and that the addition of the zeolite Y layer did not create too much additional resistance for gas transport. In order to study the effect of the zeolite Y/Biomax PES substrate on membrane separation performance with the selective polymer cover layer in this work, the Pebax[®]/PEG-200 membranes were prepared on the bare Biomax PES support with the same procedures described in Section 2.2.2 and characterized for comparison (Fig. 20).

The membrane prepared with 25 wt% PEG-200 on the bare Biomax PES support showed a slightly lower CO₂ permeance in comparison with that prepared on the zeolite Y/Biomax PES substrate (207 GPU vs. 233 GPU as shown in Fig. 20). However, this difference became greater, when the content of PEG-200 was increased to 50 wt% (521 GPU vs. 610 GPU). On the other hand, Fig. 21 shows that the thickness of the polymer layer (50 wt% PEG-200) prepared on the bare Biomax PES support was similar to that prepared on the zeolite Y/Biomax PES substrate (Fig. 19), which suggested that the mass transfer resistances for CO₂ transport were comparable in both cases. In addition, the SEM images revealed that the membrane prepared on zeolite Y/Biomax PES substrate showed a much sharper interface between the selective layer and the substrate (Fig. 19) compared to that prepared on the bare Biomax PES support (Fig. 21), which indicated more penetration of the selective layer to the underlying support. Therefore, the reduction of CO₂ permeance with the bare Biomax PES support might result from the penetration

of PEG-200 into the large pores of this substrate (Table 2), which became more pronounced at the high PEG-200 content.

In comparison with the bare Biomax PES support, the packing of the nanoparticles (40 nm particle size) could reduce the apparent pore size on the zeolite Y/Biomax PES substrate to prevent the penetration of small PEG-200 molecules. With the assumption that the zeolite Y nanoparticles are identical spheres with a diameter of 40 nm, the approximate interparticle pore size and surface porosity could be estimated by using the 2-dimensional square and 2-dimensional hexagonal close-packing configurations, respectively. Table 4 summarizes the results from these two configurations. In reality, the zeolite Y layer might not be perfectly close-packed, which could result in slightly larger pore size and porosity. In this case, the pore size of the zeolite Y/Biomax PES substrate could still be much smaller than that of the bare polymer support, while the surface porosity could be comparable or even larger. As a result, the additional thin zeolite Y layer could minimize the penetration of small molecules without creating a significant additional resistance for CO₂ transport.

Fig. 22 summarizes the data of CO₂/N₂ selectivity vs. CO₂ permeance reported in the literature [42-48] and that obtained from this work. The multilayer polymer/zeolite Y composite membrane showed a higher CO₂ permeance than most of the membranes reported in the literature. However, the membranes developed by MTR [8] and GKSS [9] were prepared with polymers of high molecular weight, which enabled the fabrication of defect-free ultra-thin membranes resulting in high CO₂ permeance. For example, the membrane thickness reported in [9] could be less than 100 nm. The synthesis of novel polymer with high molecular weight and good CO₂ affinity is being developed in our group to further increase the CO₂ permeance of the composite membrane.

This concept of multilayer polymer/zeolite Y composite membrane structure has provided the basis for high performance membranes (CO_2/N_2 selectivity of greater than 140 and CO_2 permeance of about 1100 GPU) with the selective polymer cover layer containing amino groups from our recent work. This work has been accepted for publication [49].

4. Conclusions

In order to utilize the advantages from both the polymeric and inorganic materials for post-combustion CO_2 capture from flue gas, different commercial polymer supports were investigated for their potentials to serve as the substrate for the deposition of zeolite Y nanoparticles (40 nm particle size) to form a crack-free zeolite Y seed layer on the flexible polymer support. The effects of the zeolite Y dispersion concentration and the deposition procedure were studied for these polymer supports to obtain a uniform zeolite Y seed layer. The zeolite Y nanoparticles were successfully deposited onto Biomax PES and TM10 PVDF supports with complete coverage by the vacuum-assisted dip deposition approach with 0.09 wt% zeolite Y dispersion at pH 7.

Both SEM and optical microscope analyses were employed to verify the surface coverage. AFM analysis indicated that the surface of the polymer support became smoother after the deposition of zeolite Y nanoparticles. Instead of the zeolite Y/TM10 PVDF substrate, the zeolite Y/Biomax PES substrate was selected for the synthesis of the membrane of the multilayer composite structure due to its smoother surface.

The Pebax[®]/PEG-200 membranes with different contents of PEG-200 were prepared on both the zeolite Y/Biomax PES substrate and bare Biomax PES support by spin coating. The zeolite Y/Biomax PES substrate could prevent the penetration of PEG-200, which resulted in higher

CO₂ permeance. A CO₂ permeance of 745 GPU with a CO₂/N₂ selectivity of 25.4 was obtained with this membrane of the multilayer composite structure when it was tested using 20% CO₂ and 80% N₂ at 57°C and ambient pressure.

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Nomenclature

x_i	molar fraction of component i in the retentate stream
x_j	molar fraction of component j in the retentate stream
y_i	molar fraction of component i in the permeate stream
y_j	molar fraction of component j in the permeate stream
P_i	permeance of component i
$P_{e,i}$	permeability of component i
l	membrane thickness

J_i steady-state flux of component i

Δp_i partial pressure difference of component i across the membrane

Greek letters

α_{ij} selectivity of component i over component j

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Table 1. Test conditions for gas permeation measurements.

Feed Gas Composition	20% CO ₂ and 80% N ₂
Feed Gas Flow Rate	60 cm ³ /min
Sweep Gas Flow Rate	30 cm ³ /min
Retentate Pressure	1.6 psig
Permeate Pressure	1.2 psig
Temperature	57°C

Table 2. Surface morphologies of different polymer supports.

Polymer Support	Average Pore Size (nm)	Porosity (%)
Biomax PES	72.0	15.8
TM10 PVDF	55.2	11.5
NL PSF	12.1	5.3

Table 3. Surface roughness of different polymer supports before and after zeolite Y deposition.

Polymer Support	Zeolite Y Deposition	Average Surface Roughness (nm)
Biomax PES	No	17
	Yes	11
TM10 PVDF	No	46
	Yes	25

Table 4. Estimated interparticle pore sizes and surface porosities of zeolite Y 40-nm particles/Biomax PES substrate.

Configuration	Interparticle Pore Size (nm)	Surface Porosity (%)
Square Close-Packing	16.5	21.5
Hexagonal Close-Packing	6.2	9.4
Average	11.4	15.4

Figure captions

Fig. 1. Schematic of multi-layer inorganic/polymer composite membrane.

Fig. 2. Zeolite Y structure with 1.2 nm super-cages connected by 0.74 nm windows.

Fig. 3. Schematic of the vacuum-assisted dip deposition apparatus.

Fig. 4. Schematic of the gas permeation apparatus.

Fig. 5. SEM images of 300 kDa Biomax PES surface: (a) 80,000 X magnification and (b) 20,000 X magnification.

Fig. 6. SEM images of Biomax PES surfaces with multiple times of depositing 0.001 wt% zeolite Y dispersion: (a) one time, (b) five times, and (c) ten times.

Fig. 7. SEM images of Biomax PES surfaces deposited with different zeolite Y dispersion concentrations: (a) 0.01 wt%, (b) 0.05 wt%, (c) 0.09 wt%, and (d) 0.12 wt%.

Fig. 8. Optical microscopic images of Biomax PES surfaces: (a) before zeolite Y deposition and (b) after zeolite Y deposition with 0.09 wt% dispersion.

Fig. 9. SEM images of TM10 PVDF surface: (a) 80,000 X magnification and (b) 35,000 X magnification.

Fig. 10. SEM images of TM10 PVDF surfaces deposited with different zeolite Y dispersion concentrations: (a) 0.07 wt%, (b) 0.09 wt%, and (c) 0.12 wt%.

Fig. 11. Optical microscopic images of TM10 PVDF surfaces: (a) before zeolite Y deposition and (b) after zeolite Y deposition with 0.09 wt% dispersion.

Fig. 12. SEM image of NL PSF surface (150,000 X magnification).

Fig. 13. Optical microscopic images of NL PSF surfaces deposited with different zeolite Y dispersion concentrations: (a) 0.09 wt%, (b) 0.12 wt%, and (c) 0.15 wt%.

Fig. 14. AFM images of Biomax PES surfaces: (a) before zeolite Y deposition and (b) after zeolite Y deposition with 0.09 wt% dispersion.

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Fig. 16. SEM image of the cross-section of zeolite Y/Biomax PES substrate.

Fig. 17. SEM images of zeolite Y/Biomax PES substrate surfaces: (a) without and (b) with Pebax[®]/PEG-200 cover layer (50 wt% PEG-200).

Fig. 18. Effect of PEG-200 content on the performance of the Pebax[®]/PEG-200 membrane on zeolite Y/Biomax PES substrate.

Fig. 19. SEM image of the cross-section of the Pebax[®]/PEG-200 layer (50 wt% PEG-200) on zeolite Y/Biomax PES substrate.

Fig. 20. Comparison of CO₂ permeances between the membranes prepared on different substrates.

Fig. 21. SEM image of the cross-section of the Pebax[®]/PEG-200 layer (50 wt% PEG-200) on Biomax PES support.

Fig. 22. CO₂/N₂ separation performances of membranes reported in the literature [8,9,42-48] and obtained from this work.

Figures

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