CO₂ Separation with Polymer/Aniline Composite Membranes

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Abstract: Polymer composite membranes containing aniline were prepared for CO₂/N₂ separation. Aniline was selected for high separation performance as an additive containing both the benzene ring to interfere with gas transport and an amino group that could induce the accelerated transport of CO₂ molecules. As a result, when aniline having both a benzene ring and an amino group was incorporated into polymer membranes, the selectivity was largely enhanced by the role of both gas barriers and CO₂ carriers. Selective layers coated on the polysulfone were identified by scanning electron microscopy (SEM) images and the interaction with aniline in the polymer matrix was confirmed by FT-IR spectroscopy. The binding energy of oxygen in the polymer matrix was investigated by XPS, and the thermal stability of the composite membrane was confirmed by TGA.

Keywords: CO₂; separation; facilitated transport; carrier

1. Introduction

Increasing CO₂ emissions in the environment is leading to global warming, which has become a major concern today [1,2]. Excessive greenhouse gases in the atmosphere cause a variety of environmental problems, such as constant rise in sea level, sea storms, and increased flooding [3,4]. Of the greenhouse gases, CO₂ is a major cause of global warming, and alone accounts for about 64% for the deterioration of the greenhouse effect [5]. Thus, the efforts to solve these problems and reduce CO₂ have been researched and reported under various categories such as absorption and adsorption technology [6–8].

However, the development of more efficient CO₂ separation processes has remained only of interest in industrial and academic research, although absorption or adsorption-based processes have been widely used in the industrial field for CO₂ separation. Especially, membrane-based technology has acquired much attraction recently. It can be utilized in important applications including pure gas supply, natural gas separation (CH₄/CO₂), and CO₂ capture (H₂/CO₂ and CO₂/N₂) [9,10]. In addition, several advantages, such as easy operation, reliability, environmental friendliness, low cost and energy consumption, are attractive as reducing technology for greenhouse gases. However, for the case of gas separation, gas transport through polymer membranes follows a solution–diffusion mechanism, but the trade-off has been observed between gas permeability and selectivity. Thus, the performance limitation called “Robeson Upper Bound” exists [11]. Due to these limitations [12], facilitated transport membranes have been considered as an effective alternative to overcome this limitation in CO₂ separation processes [13–15]. Facilitated transport is to add a carrier that reacts only with a specific material in an existing medium, so that the transport of a specific material becomes very fast because a carrier-mediated transport is added to the existing fickian transport.

Recently, a growing number of groups has been investigating the facilitated transport applied for CO₂ separation. Dai et al. reported that polyethylene glycol dimethyl ether (PEGDME, Mn-250 and 500)
of different molecular weights was added as a CO$_2$-philic additive to Nafion-based membranes [16]. The addition of 40 wt % PEGDME (Mn-250) to the Nafion matrix showed 57.4 barrer of CO$_2$ permeability in the dry state. It was 36-fold higher than the original Nafion, and the CO$_2$ capture performance was improved. Kline et al. reported on PEO-based crosslinked membranes by systematically varying Al(SG) for enhancing CO$_2$ transport. The carboxyl group of 5-hydroxy-isophthalic acid produced a dipole–dipole interaction with the negative carboxylate group of 5-hydroxy-isophthalic acid. These secondary amines provided adequate adsorbate–adsorbent interaction with regard to selective CO$_2$ separation. The addition of 40 wt % PEGDME (Mn-250) to the Nafion matrix showed 57.4 barrer of CO$_2$ permeability. Conclusively, the selectivity of CO$_2$ increased from 1.8 to 23 and CO$_2$ permeability of 573 barrer were observed. The ideal selectivity 32.4 of CO$_2$ to N$_2$ and the CO$_2$ permeability of 573 barrer were observed. The CO$_2$ molecule to increase the solubility of the CO$_2$ while the benzene rings as barrier effect could reduce N$_2$ transport, resulting in high permeability and high selectivity. Furthermore, a solid state membrane is more desirable for practical application since the liquid state such as ionic liquids showed disadvantages such as penetration into the support, resulting in disadvantages such as penetration into the support, resulting in disadvantages such as penetration into the support, resulting in disadvantages such as penetration into the support, resulting in disadvantages such as penetration into the support.
decreased permeability. In this study, we selected poly(vinyl alcohol) (PVA) containing a hydroxyl group as hydrophilic functional group. It was thought that the PVA as polymer matrix could not easily penetrate into the support when coated on a polysulfone porous support, and the OH groups included could disperse the additives with the effect of enhancing the solubility of CO₂ molecules. Especially, aniline as an additive was utilized since it was expected that the benzene ring could generate a barrier effect and the amino groups could act as carrier for facilitated transport. Therefore, aniline would help the CO₂ molecule pass through the membrane.

2. Materials and Methods

2.1. Materials

Poly(vinyl alcohol) (PVA) (Mₗ = 85,000–124,000) and aniline were purchased from Sigma-Aldrich (Saint Quentin Fallavier, France). Distilled water was used as the solvent. The permeance measurement was followed as described previously [29].

2.2. Preparation of Membrane

The membranes were prepared using PVA, aniline and distilled water. First, the PVA was added together with distilled water to make a 3 wt % solution. Then aniline was added in various mole ratios. To dissolve evenly the solutes, the solution was stirred one day at 95 °C in an oil bath. The final solution was coated onto polysulfone microporous membrane supports (Toray Chemical Korea Inc., Seoul, Korea) using an RK Control Coater (Model 202, Control Coater RK Print-Coat Instruments Ltd., Litlington, UK). The coated membrane was placed in a vacuum oven to remove the solvents for 3 h.

2.3. Permeance Measurements

All gas flow rates refer to gas permeance measurements using a bubble flow meter at room temperature and 2 atmospheres. The unit of gas permeance is GPU and 1 GPU = 1 × 10⁻⁶ cm³ (STP)/(cm² s cmHg).

2.4. Characterization

The thickness of the selective layer was investigated using scanning electron microscopy (SEM, JEOL, JSM-5600LV). Fourier transform infrared measurements (FT-IR) were performed on a VERTEX 70 FT-IR spectrometer (BRUKER, Billerica, MA, USA). IR spectra were acquired in the range of the wavenumber from 4000 to 400 cm⁻¹, and 16–32 scans were averaged at a resolution of 4 cm⁻¹. The weight loss of the composite membrane in flowing N₂ was confirmed using thermogravimetric analysis (TGA, TGA Q50, TA Instrument, New Castle, DE, USA) at a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) data were acquired using a PHI 5000 Versa Probe (Ulvac-PHI, Japan) photoelectron spectrometer. This system was equipped with an Al Ka μ-focused monochromator (1486.6 eV) and the detection limit was 0.5 at %. The carbon (C 1s) line at 285.0 eV was used as a reference for determining the binding energies of the O atom.

3. Results

3.1. Scanning Electron Microscopy (SEM) Images of the Membrane

The SEM image of polysulfone, a macroporous support, and polysulfone coated with PVA/aniline revealed the presence and thickness of a selective layer of composite membrane. The sponge-like structure of the support was effective for gas permeation (shown in Figure 1a). In addition, as Figure 1b, the PVA/aniline composite membrane had a selective layer, which was a section that contributed to increasing the selectivity of the gas. The average thickness of the selective layer was about 4.3 µm, filling the pores of the support and generating facilitated transport of CO₂.
3.2. Thermogravimetric Analysis (TGA)

The thermal properties of neat PVA, neat aniline, 1:0.15 PVA/aniline composite membranes were measured through TGA as shown in Figure 2. Figure 2 exhibits the multiple-steps of degradation. Evaporation of the solvent and partial aniline amount occurred from room temperature to about 100 °C. The change of curve in the next step to 235 °C was generated by the melting point of the PVA molecule, and the decomposition around 430 °C was the stage at which the hydroxy group decomposed from the PVA chains. Finally, degradation of the polymer backbone was observed after about 700 °C. When aniline was added to the polymer, the intermolecular force of PVA was reduced by the aniline, and chain-packing was prevented compared to the pure polymer. These steric effects increased the free volume and decreased the thermal stability. These increased free volumes were expected to enhance the gas permeability through increased diffusivity.

![Figure 1. SEM image of (a) neat polysulfone and (b) 1/0.15 PVA/aniline composite membrane.](image1)

![Figure 2. TGA graph of neat PVA, neat aniline and 1/0.15 PVA/aniline composite membranes.](image2)

3.3. X-ray Photoelectron Spectroscopy (XPS)

The change in the chemical environment of the O atom in the PVA/aniline composite was analyzed by XPS. As shown in Figure 3, an increase of binding energy for the O atom from 532.72 to 532.85 eV was observed. This increase in binding energy was due to the decrease in the electron density of O atoms, suggesting that there was interaction between the H atom of aniline and the O atom of PVA. In C–O–H bonds of the PVA chain, O was partially negatively charged and formed hydrogen-bonds...
with N–H of aniline. These interactions caused the electron density of O to be diminished, resulting in the increase of the binding energy.

![XPS spectra showing binding energy of oxygen in neat PVA and 1/0.15 PVA/aniline composite membranes.](image)

**Figure 3.** XPS spectra showing binding energy of oxygen in neat PVA and 1/0.15 PVA/aniline composite membranes.

### 3.4. FT-IR

As shown in Figure 4, to identify the complexation behavior of the functional groups, the FT-IR spectra of neat PVA, neat aniline, and 1:0.15 PVA/aniline composite membrane were measured. Figure 4a shows the peak of the C–O bond in PVA. As shown in Figure 4a, the main peaks of the C–O bond in neat PVA were 1058 and 1091 cm$^{-1}$. The C–O bond of PVA was weakened by the hydrogen bond with aniline, and as a result, the peak was shifted from 1091 to 1086 cm$^{-1}$. Figure 4b shows the IR spectra of the OH bond of PVA, where a change in peak was not observed. The deconvoluted area % for each component is shown in Figure 5 and Table 1. For membranes with aniline embedded in PVA, the area of the left peak increased from 74.17% to 85.25%. This result showed that the strength of the O–H bond was decreased by hydrogen bonding between PVA and aniline. Thus, new interactions between the O atom of PVA and the H atom of aniline, and the H atom of PVA and the N atom of aniline were created as shown in Figure 6, and it was also found that aniline was successfully inserted into the polymer matrix.

![FT-IR spectra of neat PVA and 1/0.15 PVA/aniline composite membranes: (a) C–O bond and (b) O–H bond.](image)

**Figure 4.** FT-IR spectra of neat PVA and 1/0.15 PVA/aniline composite membranes: (a) C–O bond and (b) O–H bond.

### Table 1.

| Peak (cm$^{-1}$) | Area (%) |
|-----------------|----------|
| Neat PVA        | 3277.43  |
| 1/0.15 PVA/aniline composite membrane | 3268.59 |

*Note: The data in Table 1 are deconvoluted area percentages for each component in the OH bonding region.*
Figure 4. FT-IR spectra of neat PVA and 1/0.15 PVA/aniline composite membranes: (a) C–O bond and (b) O–H bond.

Figure 5. The deconvolution of OH bonding in (a) neat PVA and (b) 1/0.15 PVA/aniline composite membranes. (red color is original data and green color is the deconvoluted data for each regions)

Table 1. The peak and area % of OH bonding in PVA.

|                  | Peak (cm$^{-1}$) | Area (%) |
|------------------|------------------|----------|
| Neat PVA         | 3277.43          | 74.17    |
| 1/0.15 PVA/aniline composite membrane | 3268.59          | 85.25    |

Figure 6. Expected interaction of PVA with aniline.

3.5. Separation Results

Figure 7 shows the selectivity of CO$_2$ according to the mole ratio of aniline added to neat PVA. Neat PVA membrane had almost no selectivity for CO$_2$ at 1.1 and permeance was 0.9 GPU. In contrast, the PVA/aniline composite membrane showed the best performance with CO$_2$ permeance of 0.8 GPU and selectivity of 83 at 1:0.15 mole ratio of PVA/aniline. These results were obtained through repeated experiments of at least three times, and it was confirmed that the performance was maintained for up to 6 h.
This enhanced separation performance meant that aniline had a special role. The first effect was the role as a carrier for facilitated transport. The amino group of the aniline had a basic property that could accelerate CO\textsubscript{2} transport as a reversible reaction. In particular, CO\textsubscript{2} molecules, which were originally of linear structure, could give a bent-shape when complexed with the amino group in aniline. The second factor was the barrier effect caused by the benzene ring. The benzene ring had a high electron density, meaning the gas molecules could not be permeated [30]. In addition, aniline could be readily dispersed in the polymer matrix by the interactions with PVA. As a result, facilitation transport occurred in the PVA/aniline composite membrane, as both the solubility and the diffusivity of the CO\textsubscript{2} molecule increased simultaneously by facilitated transport of the fixed carriers in the solid-state. Data showing the difference between the permeability of the pure polymer and PVA/aniline is not distinguishable, and it seems that aniline acted more as the second factor than the first factor. Scheme 1 shows the separation mechanism of the PVA/aniline composite membrane. After coating PVA/aniline on the porous support of polysulfone, the solubility of CO\textsubscript{2} increased because aniline in the polymer matrix caused CO\textsubscript{2} to be largely soluble through the membrane due to facilitated transport. On the other hand, as the transport path of N\textsubscript{2} increased due to the barrier effect of the benzene ring, the permeability of N\textsubscript{2} decreased, resulting in the enhancement of selectivity for CO\textsubscript{2}.

However, it was observed that the selectivity decreases after a 0.15 mole ratio. These results were caused by the permeance of all gases enhanced due to the aggregation phenomena of aniline. Above 0.2 mole ratio, a collapsed polysulfone support was observed due to the solvation effect of aniline, resulting in the decrease of gas permeance.

![Figure 7](Image)

**Figure 7.** Gas separation performance of PVA/aniline composite membranes. (red color is the selectivity and black square is CO\textsubscript{2} permeance).
4. Conclusions

In this work, we succeeded in providing a highly selective membrane using aniline for facilitated transport for CO$_2$ molecules. As a result, the PVA/aniline composite membrane showed a largely enhanced separation performance of about 80 times that of neat PVA membrane with 80 selectivity CO$_2$/N$_2$ in single gas permeation experiment. These results were due to both the facilitated transport and the barrier effect produced by aniline with enhanced CO$_2$ solubility by the OH groups in PVA. The chemical and physical properties of the membranes were characteristics of the membranes which were analyzed by various types of analysis equipment. As a result, it was confirmed that the free volume increase by the additive and hydrogen bonding between the polymer chain and aniline was generated for both the increase of diffusion and CO$_2$ solubility with the facilitated transport, resulting in an enhanced separation performance.

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