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Development of poly(amidoamine) dendrimer/poly(vinyl alcohol) hybrid membranes for CO_2 separation

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ABSTRACT

A novel hybrid membrane of poly(amidoamine) (PAMAM) dendrimer/cross-linked poly(vinyl alcohol) (PVA) was developed for the selective separation of CO_2 from a mixture of CO_2 and H_2. PAMAM dendrimers were incorporated into a cross-linked PVA matrix to improve CO_2 separation performance at elevated pressures. An organic metal compound di-isopropoxy-bis(triethanol aminato) titanium (Ti cross-linker) was selected as the PVA cross-linker. The characterization of PAMAM/cross-linked PVA hybrid membranes was conducted using Fourier transform infrared spectrometry/attenuated total reflectance (FTIR/ATR), wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS) spectra. Cross-linking of PVA with Ti cross-linker was confirmed by FTIR/ATR spectra. WAXD spectra showed that the relative crystallinity of PAMAM/PVA hybrid membrane decreased greatly when compared with PVA film. SAXS results indicated that PAMAM and PVA are compatible in the PAMAM/PVA hybrid membrane. To improve the CO_2 separation performance, the addition of amino acids such as glycine, proline, and 2,3-diaminopropionic acid was investigated. Separation performance was improved by addition of amino acids, such as proline. The resulting PAMAM/cross-linked PVA membrane with 5 wt.% proline addition demonstrated an high CO_2/H_2 selectivity of 38 with CO_2 permeance of 1.9×10^{-12} (m^3(STP)/(m^2 s Pa)) at CO_2 partial pressure of 560 kPa at 60 ℃. The PAMAM dendrimer/cross-linked PVA membrane shows great potential for CO_2 separation from H_2 at elevated pressures that are typically found in IGCC processes.

Keywords: Poly(amidoamine) dendrimer; Cross-linked poly(vinyl alcohol); Hybrid membrane; CO_2 separation

1. Introduction

Carbon dioxide (CO_2) capture and storage (CCS) is widely accepted as an important option for mitigating climate change [1]. The cost of CO_2 capture has been reported more than 60% of the total cost of CCS, and thus reducing the cost of CO_2 capture is critical if CCS is to be implemented [2]. Therefore, CCS requires cost-effective method for CO_2 capture for practical use. CO_2 separation by membrane is a promising technique because of its energy efficiency and simplicity to operate [3]. Membrane separation meets the demand for CO_2 separation from a pressurized gas

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stream, for example IGCC (integrated coal gasification combined cycle) process, because a higher pressure difference between feed and permeate sides of membrane will provide enough driving force for membrane separation without additional compressor or vacuum pump, and results in the cost-down of CO_2 separation.

Sirkar et al. [4–6] reported that a PAMAM dendrimer immobilized liquid membrane (ILM) demonstrates high CO_2/N_2 selectivity under atmospheric pressure. However, the dendrimer ILM had insufficient pressure tolerance for a practical use because of the flow nature of PAMAM dendrimer at or above room temperature.

To improve CO_2 separation performance at pressure difference conditions, hybrid membranes have been developed by incorporating or immobilizing of PAMAM dendrimer into a polymer matrix in our research group. We have succeeded in immobilizing the dendrimer in a cross-linked chitosan by the *in situ* modification method, and the resulting membrane system demonstrated remarkable enhancement in CO_2/N_2 separation [7–9]. However, the limited loading efficiency of PAMAM dendrimer (up to 30 wt.%) and the complicated procedures of fabrication have resulted in an alternative immobilization of the dendrimer into a suitable matrix. Recently, an effective incorporation of PAMAM dendrimer in a cross-linked poly(ethylene glycol) (PEG) obtained by photopolymerization of PEG dimethacrylate (PEGDMA) [10], and the resulting membrane showed high CO_2/H_2 separation performance.

Poly(vinyl alcohol) (PVA) has been used as the matrix of the CO_2 facilitated transport membranes because of its good compatibility with both mobile and fixed carriers, high hydrophilicity, and good film forming ability. Ho et al. reported cross-linked poly (vinyl alcohol) membranes containing glycine salts and polyethylenimine and found that both CO_2 permeability and CO_2/H_2 selectivity of the membranes increased as temperature increased in the temperature range of 50–100℃ [11].

In our previous study, a novel hybrid membrane of poly(amidoamine) (PAMAM) dendrimers/cross-linked poly(vinyl alcohol) (PVA) was developed [12]. PVA network was formed with a cross-linker in the presence of PAMAM dendrimer in aqueous media. PAMAM was successfully immobilized in cross-linked PVA matrix. The hybrid membrane showed high CO_2 separation performance with good mechanical properties, and the CO_2/H_2 selectivity exceeded 30 at 0.56 MPa of CO_2 partial pressure. However, CO_2 permeance was not high enough for a practice use. In this paper, to enhance the CO_2 permeance, effect of additives, e.g. amino acids such as glycine (Gly), proline (Pro), and 2,3-diaminopropionic acid (DAPA) was investigated to improve CO_2 separation performance. In addition, the characterization of PAMAM/cross-linked PVA hybrid membranes was conducted using Fourier transform infrared spectrometry/attenuated total reflectance (FTIR/ATR), wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering spectra (SAXS) to understand membrane structure.

2. Experimental

2.1. Materials

PVA (98 + mol% hydrolyzed; degree of polymerization: 2,000) was purchased from Wako Pure Chemical (Osaka, Japan), Ti cross-linker was obtained as a 80 wt. % isopropanol solution from Matsumoto Fine Chemical (Chiba, Japan), and PAMAM dendrimer (0th generation) was purchased as a 20 wt.% methanol solution from Sigma-Aldrich (MO, USA). Amino acids glycine, proline, and 2,3-diaminopropionic acid were purchased from Sigma-Aldrich (MO, USA). Other chemicals used were analytical grade and used as received.

2.2. Membrane preparation

Membrane preparation procedure was described in detail elsewhere [12]. In short, PVA (5 g) was added to deionized water (95 g) and refluxed at 110°C until complete dissolution giving a 5 wt.% PVA solution. A given amount of PAMAM dendrimer and amino acids were added to the PVA solution, and the mixture was stirred for 4 h at room temperature. The Ti cross-linker solution was diluted 10 times with deionized water, and the diluted Ti cross-linker solution was added into the PAMAM/amino acid/ PVA solution (PAMAM/amino acid /PVA/Ti cross-linker = 40.6/5.0/48.9/5.5 wt.%). The reaction mixture was stirred at room temperature for 30 min. The solution was then centrifuged for 15 min at 5,000 rpm using a versatile compact centrifuge (Himac CF 16RX, Hitachi, Tokyo, Japan) to remove air bubbles. A 22 g aliquot of the reaction mixture was cast on a Teflon dish (I.D.: 6.0 cm), followed by drying at room temperature for two days to evaporate the water. The resulting membrane was further dried by heating to 40 ℃ for 24 h and then to 120 ℃ for 1 h. Free-standing PAMAM/PVA hybrid membranes with a thickness of about 400 μm were thus obtained. Schematic diagram of immobilizaiton of PAMAM dendrimer in cross-linked PVA are shown in Fig. 1.

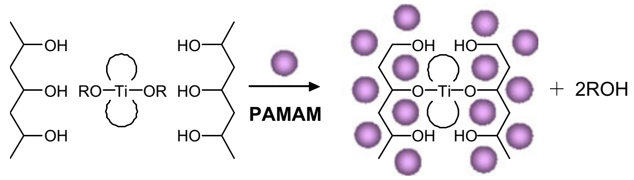

Fig. 1. Schematic diagram of immobilization of PAMAM dendrimer in cross-linked PVA with Ti cross-linker.

2.3. Membrane characterization

The chemical structure of the membranes was characterized with JASCO FT/IR 6000 a Fourier transform infrared (FTIR) spectrometer with an attenuated total reflectance (ATR) JASCO IRT-5000 (JASCO corporation, Japan). WAXD measurement was performed on RINT2000 X-ray diffractometer with The radiation source was Cu-Kα (λ: 1.5418 Å). A step size of 0.2° was used and 2 from 3° to 50° at 40 kV, 20 mA. SAXS measurement is performed on Bruker AX NanoSTAR TXS with Cu-Kα (λ: 1.5418 Å) radiation operated 30 min at 40 kV and 20 mA (Rigaku, Japan).

2.4. Gas permeation

A schematic diagram of the gas separation apparatus is shown in Fig. 2.

A CO_2/H_2 (80/20 by vol.) gas mixture was humidified at 80% relative humidity and then fed to a flat-sheet membrane cell at a flow rate of 100 ml/min. The CO_2 partial pressures of the feed side were 80, 240, 400, and 560 kPa. Dry He gas was supplied at a flow rate of 10 ml/min to the permeate side of the cell as a sweep gas to collect the permeate. The CO_2 and H_2 concentrations in both feed and permeate gases were measured by gas chromatography with a pulsed discharge detector (GC-4000, GL Sciences Inc., Tokyo, Japan). Under these experimental conditions, the pressure ratio of feed to permeate was sufficient to give the separation factor as an ideal separation factor (selectivity). Permeance, Q, and selectivity, $\alpha_{CO2/H2}$ were calculated as explained in reference [12].

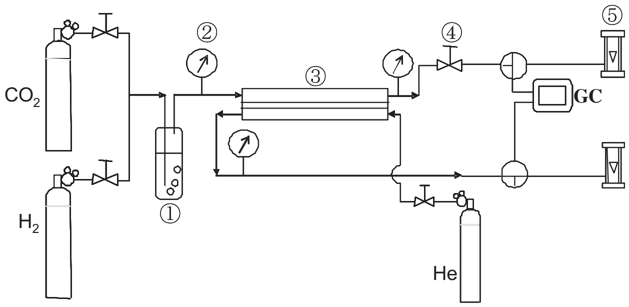

Fig. 2. Schematic diagram of gas separation apparatus. (1) Humidifier, (2) pressure gauge, (3) membrane, (4) back pressure valve, (5) bubble flow meter.

3. Results and discussion

3.1. Membrane characterization via FTIR/ATR

Fig. 3 presents the FTIR/ATR spectra of the membranes of pure PVA and cross-linked PVA with Ti cross-linker, PAMAM/cross-linked PVA hybrid membrane, and PAMAM dendrimer.

In pure PVA membrane and PAMAM, there was no peak at 1,040 cm^{-1} which attributed to the -C_{PVA}-O-Ti-O-C_{PVA}- stretch [13]. On the other hand, in the membranes prepared from the PVA cross-linked with Ti cross-linker, the 1,040 cm^{-1} peak was present. Therefore, the formation of the cross-linking of PVA by Ti cross-linker was confirmed.

3.2. Membrane characterization via WAXD

WAXD spectra are shown in Fig. 4.

WAXD spectra of PVA have sharp peaks at the values of 2 of 11.2°, 19.8°, 20.2°, and 23.1° that are typical for PVA with high crystalline. On the other hand, PAMAM/PVA hybrid membrane has broad peaks with weak intensity, indicating low crystallinity [14,15].

3.3. Membrane characterization via SAXS

SAXS curve for PAMAM/PVA hybrid membrane is shown in Fig. 5.

SAXS curve for PAMAM/PVA hybrid membrane reveals the absence of the peak indicating period structure of PVA polymer. There would be an average distance of 12 nm among PVA nanocrystallites in pure PVA [16]. These lamellar structures are plate-like with the polymer molecules folded upon themselves resulting in parallel chains perpendicular to the face of the crystal. These crystals are connected to the amorphous regions by polymer chains [17]. On the other hand, PAMAM/PVA hybrid membrane is associated with the chemical cross-linking of polymer chain by Ti cross-linker, as verified by FTIR/ATR spectroscopy. Thus, it is reasonable to assume that a significant reduction in nanocrystallites formation is due the presence of the cross-linking of PVA chains. Therefore, there is no period structure in PAMAM/PVA hybrid membrane. From these results, it was suggested that PAMAM and PVA are compatible in the PAMAM/PVA hybrid membrane.

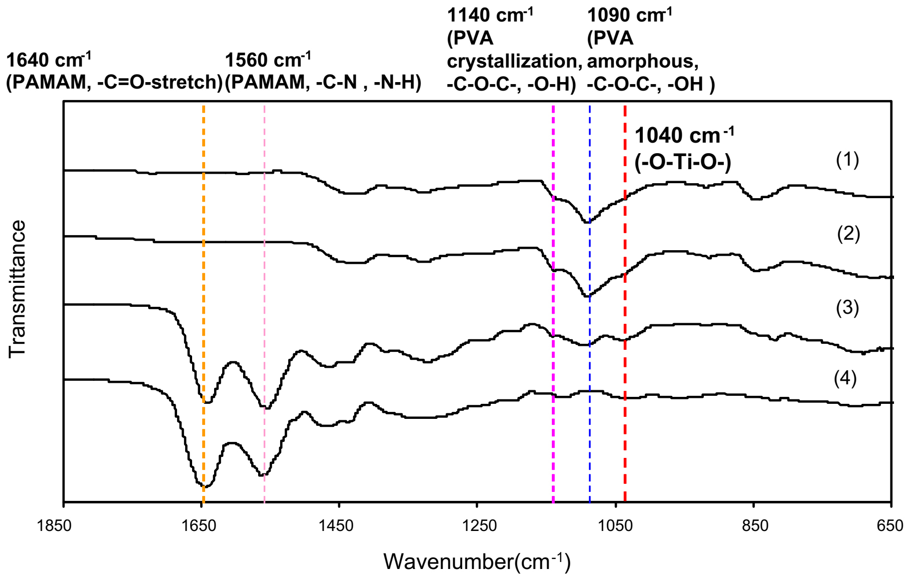

Fig. 3. FT-IR/ATR spectra of (1) pure PVA, (2) PVA/Ti cross-linker (87.5/12.5 wt.%), (3) PAMAM/PVA/Ti cross-linker (51.9/41.5 /6.6wt%) and (4) PAMAM.

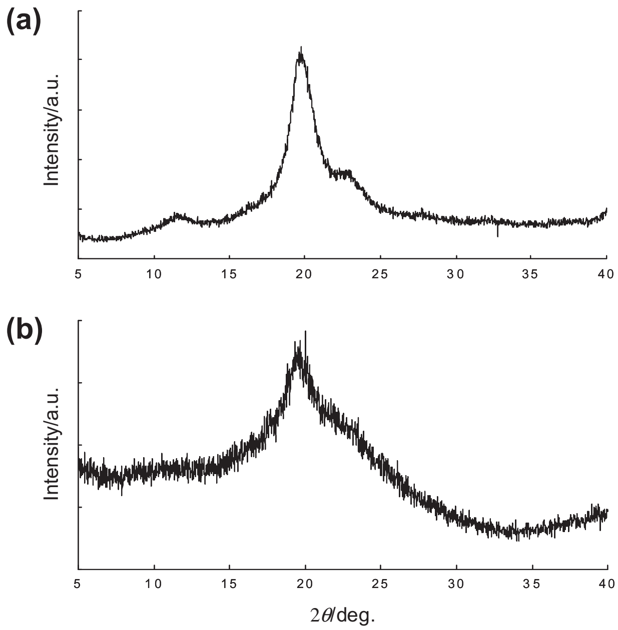

Fig. 4. XRD spectra of (a) PVA and (b) PAMAM/PV A hybrid membrane. [PAMAM] = 41.5 wt.%.

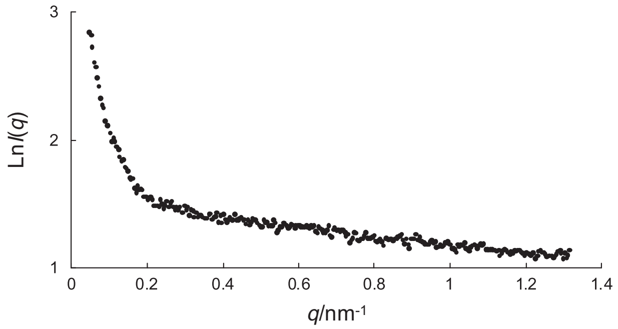

Fig. 5. Small-angle X-ray scattering spectra of PAMAM/ PVA hybrid membrane. [PAMAM] = 41.5 wt.%.

3.4. Effect of additives on CO_2 separation properties

As reported in our previous paper, PAMAM/PVA hybrid membrane showed high separation performance using pressurized gas mixture [12]. It was shown that cross-linking by Ti cross-linker was effective to show stable separation performance even under pressurized conditions. However, CO_2 permeance was not high enough to apply the membrane for the CCS. So, in this study, effect of various additives on CO_2 separation performance was investigated. Among various additives, we found that amino acids were effective to improve the CO_2 separation performance.

Effect of amino acids on CO_2 separation properties of PAMAM/PVA hybrid membrane under isobaric condition is shown in Table 1.

As shown in Table 1, amino acids were effective to increase CO_2 permeance and α_{CO_2/H_2}.

Effect of amino acids on CO_2 separation properties of PAMAM/PVA hybrid membrane under 560kPa CO_2 partial pressure is shown in Table 2.

As shown in Table 2, PAMAM/PVA hybrid membrane with Proline (Pro) as additive showed both higher CO_2 permeance and $\alpha_{CO2/H2}$ than those of the

Table 1
Effect of amino acids on CO_2 separation properties of PAMAM/PVA hybrid membrane at 80% RH and 313 K under 80 kPa CO_2 partial pressure

Additive	Q_{CO_2}/m^3 (STP) (m^2 s Pa)	Q_{H_2}/m^3 (STP)/ (m^2 s Pa)	α_{CO_2/H_2}
–	3.64×10^{-12}	7.88×10^{-14}	46
Gly	1.53×10^{-11}	2.04×10^{-13}	76
Pro	7.83×10^{-12}	1.31×10^{-13}	60
DAPA	4.39×10^{-12}	7.48×10^{-14}	59

[amino acid]=5 wt %.

Table 2
Effect of amino acids on CO_2 separation properties of PAMAM/PVA hybrid membrane at 80% RH and 313 K under 560 kPa CO_2 partial pressure

Amino acids	Q_{CO_2}/m^3 (STP) (m^2 s Pa)	Q_{H_2}/m^3 (STP) (m^2 s Pa)	α_{CO_2/H_2}
–	1.57×10^{-12}	4.91×10^{-14}	32
Gly	2.48×10^{-12}	1.94×10^{-12}	2
Pro	1.91×10^{-12}	5.07×10^{-14}	38
DAPA	4.70×10^{-13}	2.39×10^{-14}	20

[amino acid] = 5 wt.%.

membrane without additives. On the other hand, in the case of glycine (Gly) and 2,3-diaminopropionic acid (DAPA), separation performance was not improved compared with the membrane without additives under pressurized conditions. The type of the additives might has affected the pressure durability of the membranes, although further investigation is needed on this issue.

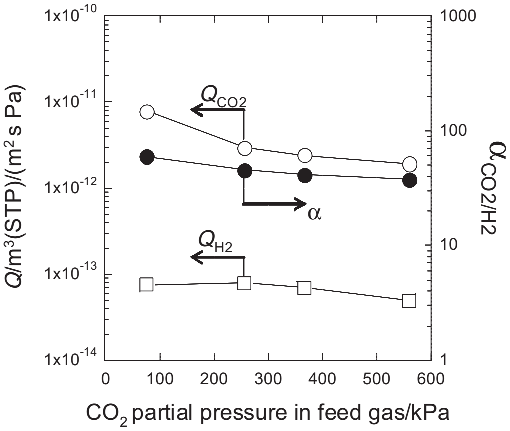

Fig. 6. Effect of CO_2 partial pressure in the feed gas on CO_2 separation of PAMAM/PVA hybird membrane containing proline (5 wt%) at 80%RH and 313 K. [PAMAM] = 41.6 wt%.

The effect of CO_2 partial pressure on CO_2 separation properties using PAMAM/Pro/PVA membrane is shown in Fig. 6.

As shown in Fig. 6 CO_2 permeance decreased to some extent with increase in CO_2 partial pressure in feed gas. However, CO_2 permeance became almost constant when CO_2 partial pressure is higher than 260 kPa. On the other hand, H_2 permeance was constant or decreased slightly as CO_2 partial pressure increased. As a result, the membrane kept high α_{CO_2/H_2} even at high CO_2 partial pressure.

4. Conclusions

PAMAM dendrimer was incorporated into a cross-linked PVA matrix to form CO_2 selective membranes with improved CO_2 separation performance at elevated pressure. PAMAM was successfully immobilized in cross-linked PVA matrix by Ti cross-linker. Cross-linking of PVA with Ti cross-linker was confirmed by FT-IR/ATR spectra. WAXD spectra showed that the relative crystallinity of PAMAM/PVA hybrid membrane decreased greatly compared with PVA film. SAXS results indicated that PAMAM and PVA are compatible in the PAMAM/PVA hybrid membrane. Separation performance was improved by addition of proline. The resulting PAMAM/cross-linked PVA membrane with 5 wt.% proline addition demonstrated a high CO_2/H_2 selectivity of 38 with a high CO_2 permeance of 1.9×10^{-12} m^3(STP)/(m^2 s Pa) at CO_2 partial pressure of 560 kPa at 60 ℃. The PAMAM dendrimer/cross-linked PVA membrane shows great potential for CO_2 separation from H_2 at elevated pressures that are typically found in IGCC processes.

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