

Article

Effect of Cross-Linking on the Mechanical and Thermal Properties of Poly(amidoamine) Dendrimer/Poly(vinyl alcohol) Hybrid Membranes for CO₂ Separation

Shuhong Duan *, Teruhiko Kai, Takashi Saito, Kota Yamazaki and Kenichi Ikeda

Research Institute of Innovative Technology for the Earth (RITE), 9-2 Kizugawadai, Kizugawa-shi, Kyoto 619-0292, Japan; E-Mails: kai.te@rite.or.jp (T.K.); saitakashi@rite.or.jp (T.S.); yamazaki@rite.or.jp (K.Y.); kenikeda@rite.or.jp (K.I.)

* Author to whom correspondence should be addressed; E-Mail: shduan@rite.or.jp;
Tel.: +81-774-75-2305; Fax: +81-774-75-2318.

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Abstract: Poly(amidoamine) (PAMAM) dendrimers were incorporated into cross-linked poly(vinyl alcohol) (PVA) matrix to improve carbon dioxide (CO₂) separation performance at elevated pressures. In our previous studies, PAMAM/PVA hybrid membranes showed high CO₂ separation properties from CO₂/H₂ mixed gases. In this study, three types of organic Ti metal compounds were selected as PVA cross-linkers that were used to prepare PAMAM/cross-linked PVA hybrid membranes. Characterization of the PAMAM/cross-linked PVA hybrid membranes was conducted using nanoindentation and thermogravimetric analyses. The effects of the cross-linker and CO₂ partial pressure in the feed gas on CO₂ separation performance were discussed. H₂O and CO₂ sorption of the PAMAM/PVA hybrid membranes were investigated to explain the obtained CO₂ separation efficiencies.

Keywords: poly(amidoamine) dendrimer; poly(vinyl alcohol); cross-linker; CO₂ separation; polymeric membrane

1. Introduction

Carbon dioxide (CO₂) capture and storage (CCS) is generally considered as an option for climate change mitigation [1]. For practical application of the CCS technology, cost-effective methods for CO₂

capture are required [2]. Many studies have focused on the development of effective CO₂ capture and separation technologies [3], with membrane separation being one of the promising solutions because of its energy efficiency and operation simplicity. Membrane separation affords CO₂ separation from a pressurized gas stream, for example through the integrated coal gasification combined cycle (IGCC) process. The high-pressure difference between the feed and permeate sides of the membrane provides sufficient driving force to conduct membrane separation in the absence of additional compressors and vacuum pumps, thus affording reduced CO₂ separation costs [4].

Sirkar *et al.* [5–7] reported that a poly(amidoamine) (PAMAM) dendrimer-immobilized liquid membrane (ILM) can achieve a high CO₂/N₂ selectivity under atmospheric pressure. However, the dendrimer ILM had insufficient pressure tolerance for practical use because of the flow nature of the PAMAM dendrimer at or above room temperature. To improve CO₂ separation performance at pressure difference conditions, hybrid membranes have been developed by incorporating or immobilizing a PAMAM dendrimer into a polymer matrix in our research group. The immobilization of the dendrimer in a cross-linked chitosan was successfully achieved by an *in situ* modification method, and the resulting membrane system demonstrated remarkable enhancement in CO₂/N₂ separation [8–10]. However, the limited loading of a PAMAM dendrimer (up to 30 wt %) and complex fabrication procedure have prompted for an alternative immobilization process. Recently, effective incorporation of a PAMAM dendrimer into a cross-linked poly(ethylene glycol) (PEG) was realized by photopolymerization of PEG dimethacrylate [11–13], and the resulting membrane showed a high CO₂/H₂ separation performance. Poly(vinyl alcohol) (PVA) has been used as a matrix to facilitate CO₂ transport through the membrane because of its good compatibility with both the mobile and stationary carriers, high hydrophilicity, and good film-forming ability. Ho *et al.* [14,15] reported cross-linked poly(vinyl alcohol) membranes containing polyallylamine, amino acid salt, and potassium hydroxide, and were claimed to contain both mobile and stationary carriers. Matsuyama *et al.* [16] reported a polyethylenimine/poly(vinyl alcohol) (PEI/PVA) blend membrane with stationary carriers. Cai *et al.* [17] reported a PAAM/PVA blend membrane with selectivities of 80 and 58 for CO₂ over N₂ and CO₂ over CH₄, respectively. In our previous studies, a novel hybrid membrane of PAMAM dendrimer/cross-linked PVA was developed [18–20]. A PVA network was formed with a Ti-based cross-linker in the presence of a PAMAM dendrimer in aqueous media. PAMAM was successfully immobilized in a cross-linked PVA matrix. In this paper, three types of organic Ti metal compounds were selected as PVA cross-linkers that were used to prepare corresponding PAMAM/cross-linked PVA hybrid membranes. Characterization of the PAMAM/cross-linked PVA hybrid membranes was conducted using nanoindentation tolerance tests and thermogravimetric analysis (TGA). The influence of the type of cross-linker and CO₂ partial pressure in the feed gas on CO₂ separation performance was investigated. H₂O and CO₂ sorption of the PAMAM/PVA hybrid membranes were examined to determine the effect of the cross-linker on the CO₂ separation properties.

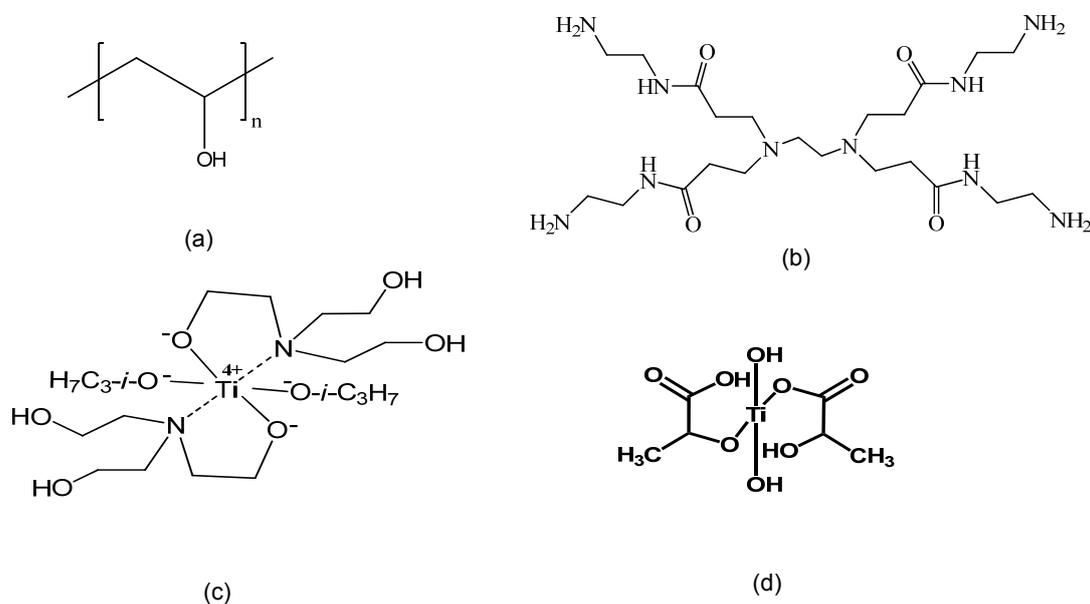
2. Experimental Section

2.1. Materials

PVA (98+ mol % hydrolyzed; degree of polymerization, *n*: 2000) was purchased from Wako Pure Chemical (Osaka, Japan), three types of Ti-based cross-linkers (TC-400, TC-300, and T-2678) were

obtained as 80 wt % isopropanol solutions from Matsumoto Fine Chemical (Chiba, Japan), and a PAMAM dendrimer (zero-generation) was purchased as a 20 wt % methanol solution from Sigma-Aldrich (St. Louis, MO, USA). The chemical structures of the materials mentioned above are shown in Figure 1. T-2678 cross-linker is not given chemical structure in detail. Other chemicals used were of analytical grade and used as received.

Figure 1. Chemical structures of PVA, PAMAM dendrimer, and Ti cross-linkers. (a) Poly(vinyl alcohol) (PVA) ($n = \sim 2000$, M_w : 88,000); (b) Polyamidoamine (PAMAM) dendrimer ($G = 0$, M_w : 516.7); (c) TC-400 cross-linker (di-isopropoxy-bis(triethanol amino)titanium, M_w : 462.4); (d) TC-310 cross-linker (di-hydroxy-bis(hydroxypropionic acid)titanate, M_w : 260.0).

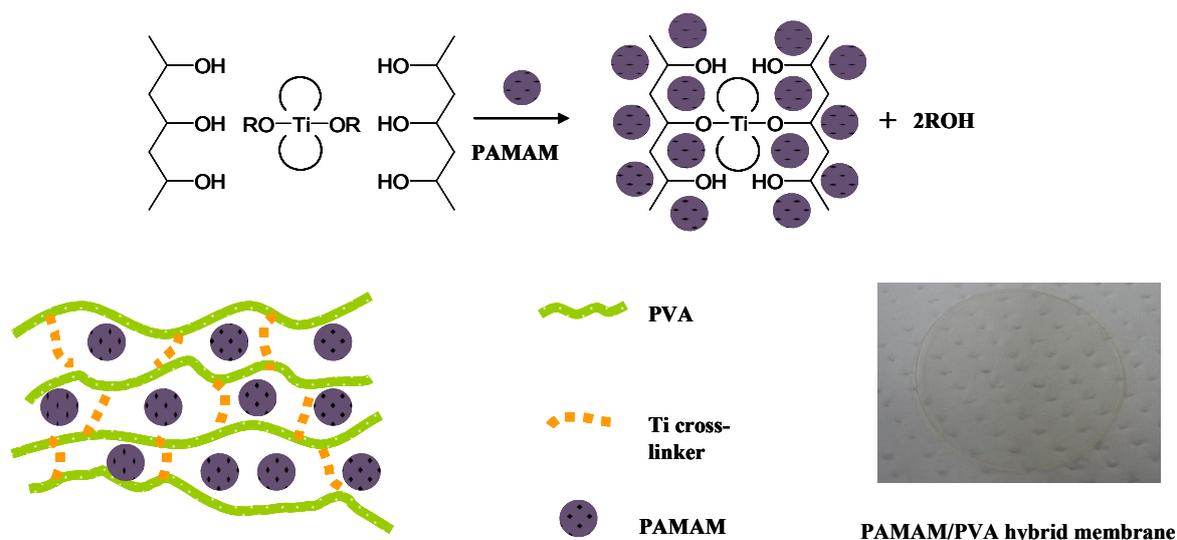


2.2. Membrane Preparation

PAMAM/PVA hybrid membranes (free-standing films) were prepared by casting a solution of PAMAM, PVA, and Ti cross-linker, at different weights, on a Teflon dish (inner diameter: 6.0 cm), as described in the reported study [6], followed by drying at room temperature for 2 days to evaporate the water.

Figure 2 shows a schematic diagram of the cross-linking process. PVA cross-linking was carried out with a Ti cross-linker in the presence of a PAMAM dendrimer in aqueous solution. The dendrimer was incorporated into the cross-linked PVA matrix to form a self-standing membrane. The representative resulting PAMAM/PVA hybrid membrane (PAMAM/PVA/TC-400 = 63.3/32.6/4.1 wt %) was transparent as seen in Figure 2.

To enhance gas permeance, thin composite membranes were prepared by casting the precursor solution of hybrid membrane onto a polyvinylidene difluoride (PVDF) support membrane. The PVDF porous support membrane (hydrophobic surface, average pore size of 0.1 μm , thickness of 120 μm , and porosity of 80%) was purchased from Millipore Com (Tokyo, Japan). The cast membrane was then dried overnight and heated at 120 $^{\circ}\text{C}$ for 10 min.

Figure 2. Schematic diagram of a PAMAM-immobilized Ti cross-linked PVA matrix.

2.3. Permeation Experiments

The schematic diagram of the gas separation experiment setup used herein was provided in reference [8]. A CO₂/H₂ (80/20 v/v) gas mixture was humidified at 80% relative humidity (RH) and then fed into a flat-sheet membrane cell at a flow rate of 100 mL/min. As reported in our previous studies, our membranes require humidity levels as high as 80% RH to achieve a high separation performance. The CO₂ partial pressures at the feed side were 80 and 560 kPa. Dry He was supplied at a flow rate of 10 mL/min to the permeate side of the cell as a sweep gas. The operating temperature was set at 40 °C. CO₂ and H₂ concentrations in both the feed and permeate gas were measured by gas chromatography. The permeance, Q , and selectivity, $\alpha_{\text{CO}_2/\text{H}_2}$, were calculated as expressed in references [8,9].

2.4. Membrane Characterization

Nanoindentation measurements of the composite membrane were performed on a Triboindenter TI-950 (Hysitron Inc., Minneapolis, MN, USA) using a Berkovich indenter (three-sided pyramidal), a quasistatic mode, and an indentation depth of ~200 nm.

TGA was carried out using a PerkinElmer Pyris 1 TGA system (PerkinELmer Japan Co., Ltd., Yokohama, Japan). Measurements were made by heating the samples from 30 °C to 300 °C under nitrogen atmosphere at a heating rate of 5 °C/min.

H₂O sorption was performed on a BELSORP-aqua3 (BEL Japan, Inc., Osaka, Japan) at 40 °C. CO₂ sorption was conducted on a BELSORP-BG (BEL Japan, Inc., Osaka, Japan) at 40 °C, 80% RH, and a pressure range of 0–800 kPa; Gas 1 was H₂O and Gas 2 was CO₂.

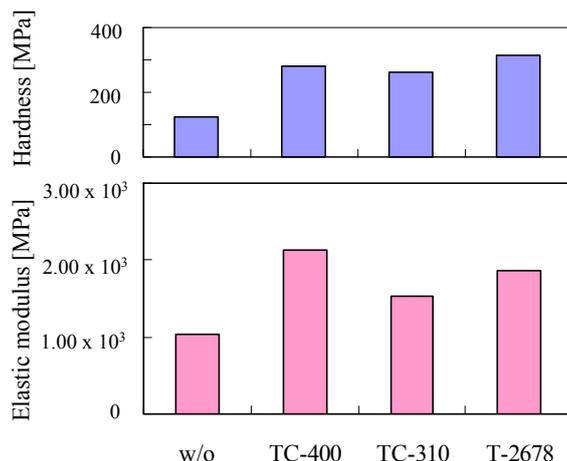
3. Results and Discussion

3.1. Nanoindentation Analysis

Figure 3 shows the nanoindentation tolerance evaluation of the membranes prepared in the absence (w/o) and presence of a cross-linking agent. PAMAM/PVA/TV-400 hybrid membrane had the highest elastic modulus. PAMAM/PVA/TC-310 hybrid membrane displayed the highest hardness.

PAMAM/PVA/T-2678 hybrid membrane had the lowest elastic modulus and hardness. However, the PAMAM/PVA hybrid membranes prepared in the presence of a cross-linking agent exhibited higher elastic modulus and hardness than those prepared in the absence of a cross-linking agent. The nanoindentation measurements suggest that cross-linking was effective to improve the mechanical strength of the PAMAM/PVA hybrid membranes.

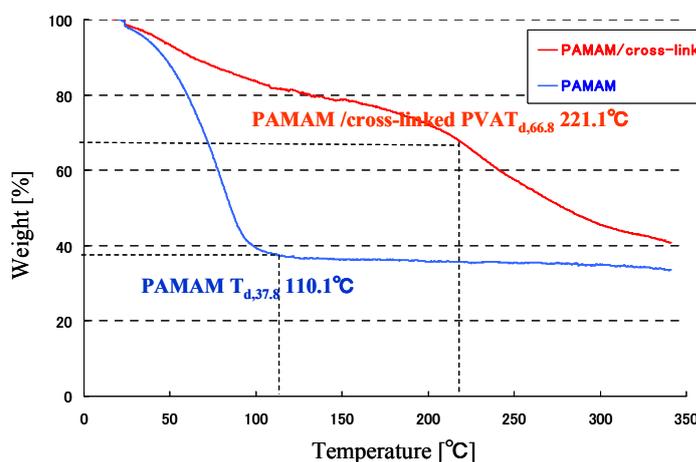
Figure 3. Nanoindentation tolerance evaluation of the hybrid membranes prepared in the absence (w/o) and presence of a cross-linking agent (TC-400, TC-310, or TC-2678).



3.2. TG Analysis

Thermal gravimetric analysis curves of the PAMAM dendrimer and PAMAM/PVA hybrid membrane (PAMAM/PVA/TC-400 = 63.3/32.6/4.1 wt %) are shown in Figure 4. The thermograph of PAMAM shows a mass loss of ~62.2% at 110 °C. The PAMAM/PVA hybrid membrane displays mass losses of ~17.6% at 110 °C and ~33.2% at 221 °C. The PAMAM-immobilized cross-linked PVA matrix shows considerably enhanced thermal stability when compared with the pure PAMAM dendrimer. The TG analysis suggests that cross-linking was effective to improve the thermal stability of the PAMAM/PVA hybrid membranes.

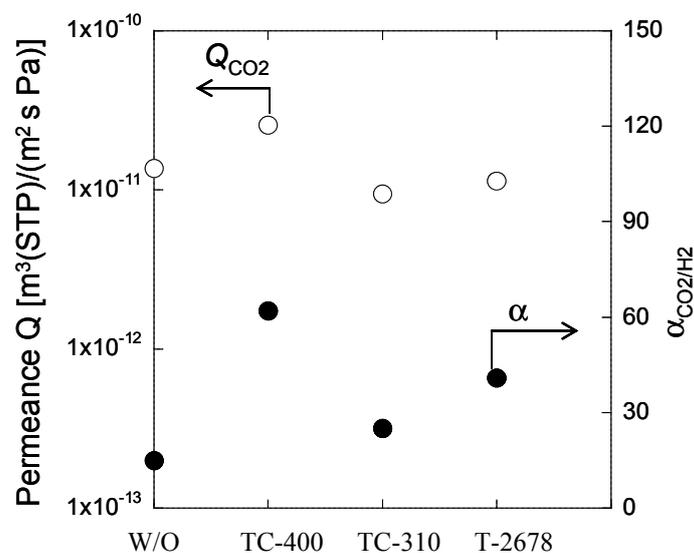
Figure 4. Thermogravimetric analysis (TGA) evaluation of the hybrid membrane and PAMAM dendrimer. TGA curves of (a) the PAMAM dendrimer; and (b) the PAMAM/cross-linked PVA hybrid membrane.



3.3. Effect of Cross-Linker on CO₂ Separation Properties

CO₂ gas separation properties of the PAMAM/PVA hybrid membranes at 40 °C and 80% RH are shown in Figure 5. The PAMAM/PVA hybrid membrane prepared in the absence of a cross-linker had a relatively low $\alpha_{\text{CO}_2/\text{H}_2}$ (CO₂/H₂ gas selectivity). Conversely, the PAMAM/PVA/TC-400 hybrid membrane showed the highest CO₂ permeance (Q_{CO_2}) and $\alpha_{\text{CO}_2/\text{H}_2}$. The PAMAM/PVA hybrid membranes prepared in the presence of cross-linking agents TC-310 and T-2678 had lower Q_{CO_2} values when compared with that of membranes prepared in the absence of a cross-linking agent; however, the former hybrid membranes displayed higher $\alpha_{\text{CO}_2/\text{H}_2}$ values. Three types of cross-linkers were used to improve the mechanical strength and thermal stability of the PAMAM/PVA hybrid membranes. Furthermore, although the cross-linking structure did not improve CO₂ permeance (e.g., PAMAM/PVA/TC-310 and PAMAM/PVA/T-2678 hybrid membranes. Figure 5), the cross-linking structure efficiently reduced H₂ permeance, thus resulting in improved CO₂/H₂ selectivity. Regarding the PAMAM/PVA/TC-400 hybrid membrane, the cross-linking structure was more effective in improving CO₂ permeance, owing to the presence of the ethanol amino groups in TC-400 that would promote CO₂ sorption.

Figure 5. Effect of cross-linker on CO₂ separation properties of PAMAM/cross-linked PVA membranes (thickness: 50 μm) at 80 kPa CO₂ partial pressure and 80% relative humidity (RH).



To further investigate the effect of the ethanol amino groups on facilitating CO₂ sorption, H₂O and CO₂ sorption onto the membranes were examined and the results are shown in Figures 6 and 7. The PAMAM/PVA/TC-400 hybrid membrane showed higher H₂O and CO₂ sorption when compared with the hybrid membranes prepared with the other two Ti cross-linkers. Consequently, the PAMAM/PVA/TC-400 hybrid membrane showed higher CO₂ permeance and selectivity.

Figure 6. Effect of cross-linker on water sorption properties of the PAMAM/cross-linked PVA membranes at 40 °C.

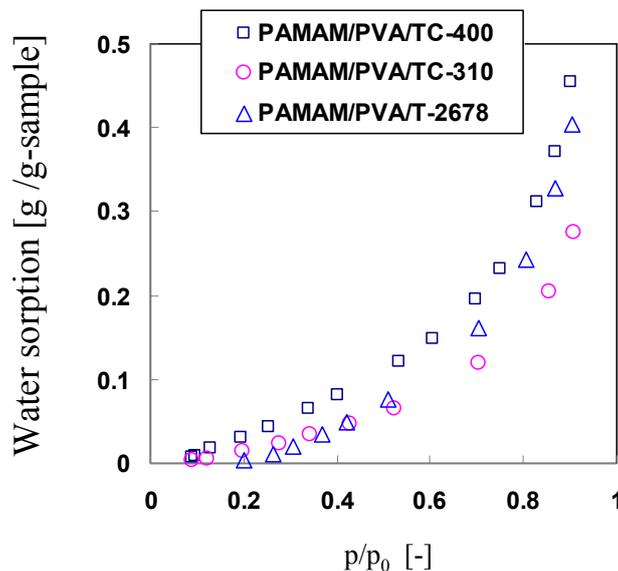
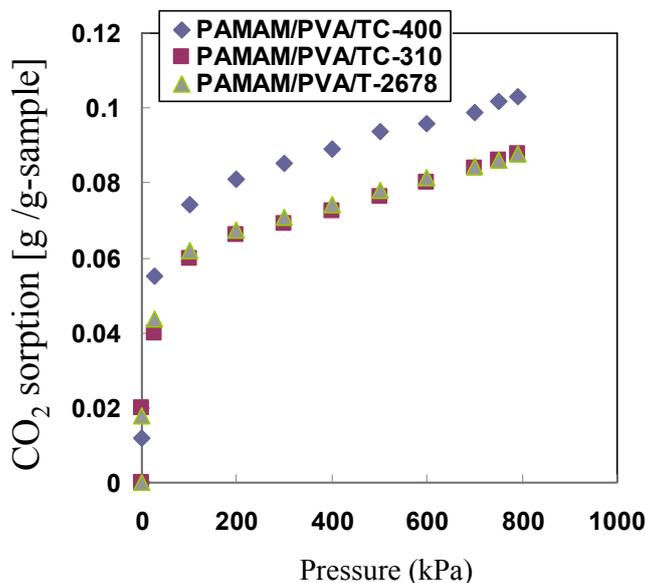


Figure 7. Effect of cross-linker on CO₂ sorption properties of the PAMAM/cross-linked PVA membranes at 40 °C.



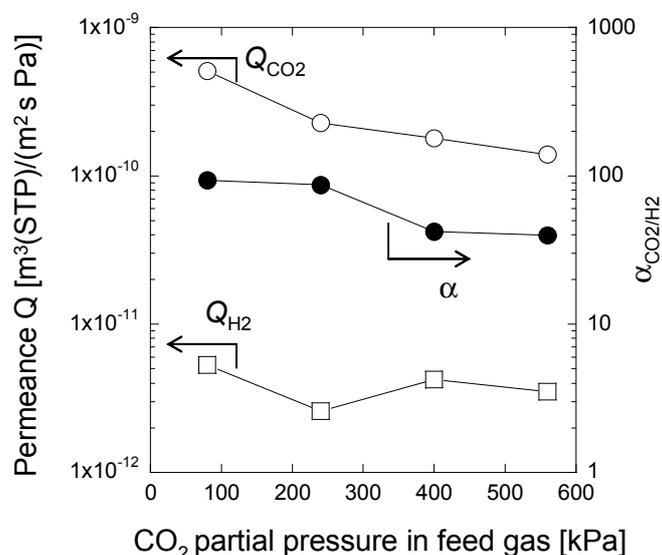
3.4. Effect of CO₂ Partial Pressure on CO₂ Separation Properties

The effect of CO₂ partial pressures on CO₂ separation properties using the composite membrane of smaller thickness prepared by casting precursor solution of PAMAM/PVA/TC-400 onto a PVDF support membrane is shown in Figure 8. In general, as observed, CO₂ permeance decreased with increasing CO₂ partial pressures in the feed gas. Conversely, H₂ permeance was relatively constant and only decreased slightly as CO₂ partial pressure increased. As a result, the membrane showed high Q_{CO_2} ($1.1 \times 10^{-10} \text{ m}^3 \text{ (STP)/(m}^2 \cdot \text{s} \cdot \text{Pa)}$) and α_{CO_2/H_2} (39) even at a high CO₂ partial pressure (*i.e.*, 560 kPa).

A decrease in the permeance of CO₂ as pressure increases is typically observed when gas separation takes place via an improved transport mechanism process [14,16], as indicated by the CO₂ sorption

behaviors. CO₂ sorption values increased from 0 to 0.075 g/g-membrane with increasing CO₂ partial pressures from 0 to 100 kPa, followed by a further increase from 0.075 to 0.094 g/g-membrane with increasing CO₂ partial pressures from 100 to 600 kPa. CO₂ sorption was facilitated by interactions between PAMAM dendrimer and CO₂ molecules. CO₂ sorption rates decreased as pressure increased. Moreover, CO₂ sorption sites in the membrane do not increase. As mentioned above, permeance of CO₂ decreased with increasing gas partial pressures. Conversely, H₂ sorption was hindered by the PAMAM dendrimers because of the absence of CO₂ chemical affinities. H₂ transport in the membrane was independent of the gas pressure and H₂ permeance remained unchanged.

Figure 8. Effect of CO₂ partial pressure in the feed gas on the CO₂ separation properties of the PAMAM/cross-linked PVA composite membrane at 90% RH and 40 °C.



4. Conclusions

PAMAM was successfully immobilized in a cross-linked PVA matrix using three types of Ti cross-linkers to form PAMAM/cross-linked PVA hybrid membranes. The nanoindentation and TG analyses demonstrated that cross-linking was effective to improve the mechanical strength and thermal stability of the PAMAM/PVA hybrid membrane. CO₂ permeance and selectivity were different depending on the type of Ti cross-linker. PAMAM/PVA/TC-400 hybrid membrane showed higher H₂O and CO₂ sorption than other hybrid membranes prepared with the other Ti cross-linkers, and the highest CO₂ separation capabilities. Moreover, the PAMAM/PVA/TC-400 hybrid membrane (thickness: 1.5 μm) showed CO₂/H₂ selectivity over 30 and CO₂ permeance over 1.0 × 10⁻¹⁰ m³ (STP)/(m²·s·Pa) at 560 kPa CO₂ partial pressure. The PAMAM dendrimer/cross-linked PVA membrane shows great potential for CO₂ separation from H₂ in high-pressure applications such as the IGCC process.

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Author Contributions

Teruhiko Kai participated in its design and helped to draft the manuscript. Takashi Saito carried out the study of the effects of CO₂ partial pressure in the feed gas on CO₂ separation performance. Kota Yamazaki carried out the study of CO₂ sorption of the PAMAM/PVA hybrid membranes. Kenichi Ikeda carried out the study of the nanoindentation of the PAMAM/cross-linked PVA hybrid membranes. All authors read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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