Development and fabrication of PAMAM-based composite membrane module with a gutter layer of Chitosan/PAA polymer double network for CO₂ separation

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Abstract. To improve the CO₂ separation performance of a poly(amidoamine) (PAMAM) dendrimer composite membrane, a gutter layer of chitosan (CTS)/polyacrylic acid (PAA) polymer double network (DN) and its fabrication are proposed. In our previous studies, PAMAM-based composite membrane module with a gutter layer of cross-linked CTS showed high CO₂ separation properties from CO₂/N₂ mixed gases. In this study, CTS/PAA polymer DN was used to prepare the gutter layer instead of CTS to enhance CO₂ permeance and pressure durability of PAMAM-based composite membrane. A PAMAM dendrimer composite membrane module with a gutter layer of CTS/PAA polymer DN, which was prepared with a coating solution of CTS/PAA (CTS/PAA=1/2 molar ratio), showed a high permeance of 8.8 × 10⁻¹¹ m³ (STP) m⁻² s⁻¹ Pa⁻¹ with a high CO₂ separation factor of 10⁴ at 40 °C, pressure 550 kPa with a feed gas mixture CO₂/N₂=5/95 (vol. /vol.).

1. Introduction
The globe warming and climate changes have had widespread impacts on human and natural systems. The sea level rises, the amount of ice and snow decreases. Combustion of fossil fuels and emissions of CO₂ from industrial processes accounted for about 78% of total greenhouse gas (GHG) emissions. Reduction of CO₂ emissions is crucial task for environmental preservation and sustainable development. Many technologies are recently employed for separation and capture of CO₂ from gas mixture resulting from industrial processes [1], with membrane separation is being one of the promising solutions because of its energy efficiency and operation simplicity [2-7].

PAMAM dendrimer was reported to have excellent CO₂/N₂ selectivity as an immobilized liquid membrane for the isobaric test condition of atmospheric pressure [8]. However, this immobilized liquid membrane had insufficient pressure tolerance for practical use. In previous papers [9, 10], we have prepared stable PAMAM dendrimer composite membranes using CTS as a gutter layer by the In-situ Modification (IM) method. The PAMAM dendrimer composite membrane had high CO₂/N₂ selectivity and can afford a practical tolerance of the pressure difference of 100 kPa reasonably high. However, further improvement for CO₂ permeance and pressure tolerance is still required.

Multicomponent polymers have been the subject of great interest, since they provide a convenient supplementary properties of each other and modify the properties in order to meet specific needs [11, 12]. Among these methods, considerable interest has been devoted to the development of polymer
double networks (DN) hydrogels [13] for gas membrane separation. In our previous study, cross-linked CTS as a gutter layer had low water sorption resulting in decrease in CO\textsubscript{2} permeance. In this work, we have selected PAA having high water sorption to form double network with CTS. The CTS/PAA polymer DN used as a gutter layer of PAMAM-based composite membrane can lead to high CO\textsubscript{2} flux transfer into membrane because of high water. As a result high CO\textsubscript{2} permeance Q\textsubscript{CO2} and high CO\textsubscript{2}/N\textsubscript{2} selectivity will achieve under elevated pressure. The water sorption and mechanical strength of CTS/PAA polymer DN will be also measured and discussed.

2. Experimental

2.1. Materials
Chitosan with molecular weight (MW: 500,000) was obtained from Kimika Co. Ltd. The deacetylation ratio of CTS was 84%. Reagent grade PAMAM dendrimer (G = 0) was obtained as 20 wt. % methanol solution from Sigma-Aldrich Co. Glutaraldehyde (GA), acrylic acid(AA) and N,N-methylene-bis-acrylamide (MBA) were purchased from Tokyo Chemical Industry Co. Ltd. Japan. All other chemicals were analytical grade. Every commercial reagent was used as received.

2.2. Synthesis of CTS/PAA polymer double network and preparation of CTS/PAA polymer DN dense membrane
According to references of [9, 10], the route to prepare cross-linked CTS network 1 is shown in Figure 1. An aqueous CTS solution containing CTS (1 wt. %) as solid components with acetic acid (4 wt. %) and GA (0.1 wt. %) was used to form cross-linked chitosan network 1. CTS was cross-linked with glutaraldehyde by primary amines of the aldol reaction. Further transformations with the already cross-linked product achieved through the condensation of the amino groups of chitosan with the carbonyl groups with the formation of the products shown in Figure 1.

![Figure 1. Schematic illustration to conformation of cross-linked chitosan network 1.](image)

Accordingly, an aqueous solution containing AA (4 wt. %) and MBA (0.5 wt. %) and TEMED was used to form cross-linked poly(acrylic) acid network 2. APS was used as the cross-linker. The cross-linked CTS/PAA polymer DN dense membrane was prepared by the cast method.

![Figure 2. Schematic illustration to conformation of cross-linked poly (acrylic) acid network 2.](image)
Figure 3. Images of CTS/PAA polymer double network.

According to references of [14, 15], the reaction to prepare cross-linked PAA is shown in Figure 2. Ammonium persulfate (APS) was used as a cross-link polymerization initiator. N, N, N', N'-Tetramethylethylenediamine (TEMED) was used as a cross-link polymerization catalyst. AA (5g) was dissolved in 50ml deionized water and then added into a triple-necked flask, which was equipped with a stirring apparatus and a reflux condenser, The solution was stirred for 20 min and heated in a water bath of 70 °C under nitrogen protection. Then, a predetermined amount MBA is added into the flask and then solution was stirred. An amount of 0.25g APS, dissolved in 30 ml deionized water, and 0.10g of TEMED, dissolved in 20ml deionized water were dropped into it with 5 min of interval, added into the flask to initiate the polymerization process. The reaction was stopped after 4hr until $^1$H NMR peak of the double bond in acrylic acid disappeared. The cross-linked AA by MBA solution was obtained as cross-linked PAA network 2. Images of CTS/PAA polymer double network is shown in Figure 3.

CTS/PAA polymer double network was formed according to CTS/PAA=1/1, 1/2, 1/3 (molar ratio) by cross-linked PAA solution added into cross-linked CTS solution. Portion of the prepared CTS/PAA solution was used for PAMAM-based composite membrane module with a gutter layer of Chitosan/PAA polymer double network. Another portion of the prepared CTS/PAA solution was neutralized by NaOH to neutralization degree of 50%, poured into a Teflon Petri dish of 100×10 mm and was then dried in the oven of 40 °C for 24 hr to form CTS/PAA polymer DN dense films with 100µm thickness for measurement of FT-IR spectrum, water sorption and mechanical strength of the films.

2.3. Fabrication of PAMAM-based composite membrane module with Chitosan/PAA polymer double network and Gas separation test

PAMAM-based composite membrane module with a gutter layer of Chitosan/PAA polymer DN was prepared by the In-situ Modification (IM) method [9, 10]. The IM method was applied to prepare the PAMAM dendrimer separation layer on the PSF supporting hollow fiber. Figure 4 shows the schematic diagram of the IM method. A solution containing the membrane materials was circulated on the lumen side of the hollow fiber membrane, while the opposite (shell) side was reduced pressure using a vacuum pump. This method can be directly used to modify the surface of the substrate situated inside a module, and will be applicable to any size of membrane module, ranging from pencil to large sized commercial modules. In the IM method, if a hydrophobic porous substrate of adequate pore size and hydrophilic solution were applied, the hydrophilic solution would be unable to penetrate into the pores of the hydrophobic substrate, resulting in the formation of a gas–liquid interface at the inner surface of the substrate. Evacuating the opposite side of the substrate causes evaporation of the solvent at the interface resulting in a solute rich state, and finally the precipitation of the membrane materials at the interface.

Polysulfone (PSF) ultrafiltration hollow fiber membranes (molecular weight cut-off: 6000) were obtained from a commercial module, NTU-3250-C1R, Nitto Denko Corp. and were used as a supporting substrate of the composite membranes. The outer and inner diameters of the hollow fiber membrane were 1900 and 1100 mm, respectively. The ultrafiltration membrane obtained in a wet state was dried under ambient temperature and atmosphere, and further dried at 60 °C for 8 hr.
Three PSF hollow fibers were inserted into a module housing (length 20 cm, diameter 3/8 in.), to form pencil module shown in Figure 5, such that the effective membrane area was about 18 cm$^2$.

![Diagram of the IM method to form CO$_2$ separation membrane module.](image)

**Figure 4.** Diagram of the IM method to form CO$_2$ separation membrane module.

![Photograph of the membrane pencil module.](image)

**Figure 5.** Photograph of the membrane pencil module.

![CO$_2$ separation test with the membrane pencil module.](image)

**Figure 6.** CO$_2$ separation test with the membrane pencil module.

Un-neutralized CTS/PAA DN solution prepared in 2.2 was circulated through the lumen side of the hollow fiber membranes in the module at a linear velocity of 8 m/min for 30 min, while the shell side was evacuated with a vacuum pump at 3 kPa. The excess CTS/PAA DN solution was blown from the bore of the fiber by air, and the fibers were then heated at 60 °C for 2 hr to form a nascent CTS/PAA DN layer. The CTS/PAA DN layer was first neutralized with 0.1 M NaOH aqueous solution, then rinsed with 50 wt. % aqueous ethanol, and finally dried for 4 hr in an oven of 70 °C under nitrogen protection. to produce the desired CTS/PAA DN gutter layer on the porous surface of the PSF substrate. Conventional or novel hydroxyl PAMAM dendrimer was hybridized into the CTS/PAA gutter layer by circulating the aqueous methanol solution containing 10 wt. % of the corresponding dendrimer at a linear velocity of 8 m/min for 30 min without evacuating the shell side and then dried to form the resulting dendrimer composite membrane. PAMAM-based composite membrane module with a gutter layer CTS/PAA polymer DN was fabricated.
Test of gas membrane separation diagram setup used herein was provided in reference [6] shown in Figure 6. A CO$_2$/N$_2$ (5/95 by vol.) gas mixture was humidified at 95% of relative humidity and then fed to a pencil membrane module at a flow rate of 200 ml/min. The CO$_2$ partial pressure under atmospheric condition was 5 kPa, while it was 550 kPa when the total pressure was 30 kPa. Operating temperature was 40 °C. CO$_2$ and N$_2$ concentration in both feed and permeate gas was measured by a gas chromatography with a pulsed discharge detector (GC-4000, GL Sciences Inc., Tokyo, Japan). In this experimental condition, the pressure ratio of the feed to the permeate side was sufficiently large, and the separation factor was thus accounted as an ideal separation factor (selectivity). Permeance, $Q$, and selectivity, $\alpha_{CO2/N2}$ were calculated according to equations (5) and (6):

$$\alpha(CO_2/N_2) = \frac{Y_{CO_2}/Y_{N_2}}{X_{CO_2}/X_{N_2}}$$

$$Q_i = \frac{N_i}{A \Delta P_i \cdot t}$$

$Q_i$: permeance of gas I (m$^3$ (STP) / (m$^2$ s Pa)); $\alpha$: CO$_2$/N$_2$ separation factor (selectivity); $N_i$: total flow rate of sweep gas (m$^3$ (STP)/s); $X$ and $Y$: mole fraction of feed and permeate side, respectively; $P_f$ and $P_p$: Pressure of feed (Pf) and permeate side (Pa) respectively; $A$: Effective membrane area (m$^2$).

3. Results and discussion

3.1. $^1$H NMR spectra to confirm polymerization process of AA and MBA

$^1$H NMR spectra was used to confirm AA and MBA polymerization process. $^1$H NMR experiments were carried out using a Bruker Avance 400 (Bruker Corporation, Japan). Figure 7 shows the chart of $^1$H-NMR spectrum of the polymerization process of AA and MBA. The chemical shifts at 5.81 ppm, 6.03 ppm and 6.20 ppm are observed after 1 hr of AA and BMA reaction and peaks of Ha, Hc and Hb of AA remained. After 4 hr of AA and BMA reaction, almost no peaks of Ha, Hb, Hc of AA remained. It indicated that AA and BMA reaction completed. Further $^{13}$C NMR measurement is necessary to confirm product structure of cross-linked AA by BMA.

![Figure 7. $^1$H-NMR spectra of AA and MBA polymerization process (400 MHz, D$_2$O).](image-url)
3.2. FT-IR spectra and gel formation of cross-linked CTS, cross-linked PAA, CTS/PAA DN films

FT-IR measurements were carried out using a JASCO FT/IR 6100 (JASCO Corporation Japan). Figure 8 shows the FT-IR spectra of cross-linked CTS, cross-linked PAA, CTS/PAA DN films. The spectrum shows a broad band at 3400 ~ 3300 cm\(^{-1}\) corresponding to the associated –OH stretching vibrations of the hydroxyl groups and the peak at 1650 cm\(^{-1}\) corresponds to the N-H deformation bending of the chitosan molecule [16]. Peaks at 1454 and 1410 cm\(^{-1}\) are due to the–CH bending vibrations of the alkyl groups. These peaks are increased with CTS/PAA molar ratio decrease. The peak appeared at 1728 cm\(^{-1}\) due to C=O stretching vibration of the –COOH group of poly (acrylic acid). This peak is disappeared in CTS/PAA = 1/0. Because all peaks are appeared according to about CTS/PAA molar ratio, it could indicate that CTS/PAA DN could be formed. Since it is technically difficult to measure solid 1H NMR in the state of a polymer film, we did not measure 1H spectra of these films. Figure 9 shows the photographs of CTS, PAA and CTS/PAA mixed solution. Since (3) was formed gel state, it clearly indicates that CTS/PAA DN was formed.

![Figure 8](image)

**Figure 8.** FT-IR spectra of cross-linked CTS, cross-linked PAA, CTS/PAA DN films.

![Figure 9](image)

**Figure 9.** The photographs of 
(1) Cross-linked CTS solution,  
(2) Cross-linked PAA solution,  
(3) Cross-linked CTS / Cross-linked PAA polymer DN

3.3. Water sorption and mechanical strength properties of CTS/PAA polymer DN

Water sorption was performed on Thermo-hygrostat chamber ESPES SH-221 (ESPEC CORP., Tokyo, Japan) at 40 °C 95 % relative humidity. The water sorption was determined by the following equation:

\[
\text{Water sorption} = \frac{(W_w - W_d)}{W_d} \times 100, 
\]

where \(W_w\) and \(W_d\) are sample weights of fully water sorption and dry films, respectively. The Effect of CTS/PAA molar ratio on water sorption properties of the CTS/PAA DN dense membranes at 40 °C was shown in Table 1. The CTS/PAA=1/3 DN dense membrane showed the highest water sorption because –COOH group of PAA can form hydrogen bonds with –COOH group of one chain and the -OH group of the –COOH of a neighboring chain [17]. The result is the apparition of a polymeric network with large free spaces where the water molecules can be trapped.

![Table 1](image)
Mechanical strength was performed on tensile tester Shimadzu TRAPEZIUM 2 (Shimadzu Corporation, Japan) at chuck interval 30 mm (film width 7 to 15 mm), tensile speed 10 mm / min, load cell 1 kgf / full scale, elongation origin 0.3% / full scale at 25 °C. The Effect of CTS/PAA molar ratio on the strength properties of CTS/PAA polymer DN dense membrane was shown in Table 1. The CTS/PAA= 1/2 DN dense membranes showed the highest mechanical strength with Young's modulus 7.5 MPa. As a general PAA added into the CTS will result in a decrease in mechanical strength, the formation of CTS/PVA DN resulted in higher mechanical, that mixture structure will be more stable beyond each network if the CTS and PAA different networks will be formed interpenetrating networks or mixed matrix networks. It will be discussed in the following paper.

Table 1. Water sorption and mechanical strength properties of CTS/PAA DN dense film.

| CTS/PAA molar ratio | 1/0 | 1/1 | 1/2 | 1/3 |
|---------------------|-----|-----|-----|-----|
| Water sorption [H₂O g /g-film x 100] | 85 | 190 | 220 | 470 |
| Young’s modulus [MPa] | 5.1 | 7.2 | 7.5 | 4.0 |

3.4. Effect of CTS/PAA polymer DN with various CTS/PAA molar ratio on CO₂ separation performance of PAMAM-based composite membrane module

CO₂ separation properties as a function of total pressure of feed gas were studied with CTS/PAA=1/0, 1/1, 1/2, 1/3 membranes and the results were shown in Figure 10, 11. As observed, Q_{CO₂} increased with increasing CTS/PAA molar ratio from 1/0 to 1/2, and then decreased at feed pressure 101.6 kPa and 550.0 kPa. The mechanism model of CO₂ and N₂ transport membrane is known as the solution-diffusion model in which permeants dissolve in the membrane material and then diffuse through the membrane. Sorption of excess water leads to increase the membrane thickness and increasing the gas diffusion path. As this reason, CTS/PAA= 1/2 DN dense membranes is the optimal membrane material considering high pressure resistance together. CO₂ and N₂ transport the membrane by Selectivity CO₂ / N₂ increased with increasing CTS/PAA molar ratio from 1/0 to 1/2, and then decreased at feed pressure 101.6 kPa and 550.0 kPa. PAMAM dendrimer composite membrane module with CTS/PAA polymer DN gutter layer, which was prepared with a coating solution of CTS/PAA (CTS/PAA=1/2 molar ratio) DN, showed a high permeance of $8.8 \times 10^{-11}$ m³ (STP) m² s⁻¹ Pa⁻¹ with a high CO₂ separation factor of 104.

As shown in Figures 10 and 11, permeation and selectivity of CTS/PAA= 1/2 DN dense membranes at 40 °C and 101.06 kPa is higher than that of CTS/PAA= 1/2 DN dense membranes at 40 °C and 550 kPa, because the CO₂ partial pressure under 101.06 kPa was 5 kPa, while it was 550 kPa when the total pressure was 30 kPa. Permeance Q_{CO₂} was calculated according to equations (6), as a result, the higher CO₂ partial pressure is, the lower Q_{CO₂} is.

As shown in Figure 12 a long pencil membrane module (length: 80 cm, membrane area: 190 cm²) was used in long-term test in our previous study [18]. The conditions were a feed gas mixture of real exhaust gas at a steel manufacturing plant CO₂/N₂ (32/68 by vol.) containing saturated water vapor, a temperature of 14–25 °C and feed pressure 101.6 kPa. The result of a long-term stability test for the PAMAM dendrimer composite membrane was shown in Figure 13. The CO₂ concentration in permeate side was consistently higher than 86% for 1000 h, and the average value was 94%. Average separation factor was 33. Therefore, the PAMAM dendrimer membrane module maintained a high CO₂ separation performance for at least 1000 h at 101.6 kPa. In this study, we developed PAMAM composite membrane supported by CTS/PAA double network gutter layer to enhance the pressure durability of the membrane, long-term test will be performed and reported next paper.
Figure 10. CO$_2$ separation performance at feed pressure 101.6 kPa, 40 °C.

Figure 11. CO$_2$ separation performance at feed pressure 550.0 kPa, 40 °C.

Figure 12. Photographs of the membrane modules of commercial-sized modules. 1100 mm in length, 1 inch in diameter [18].

Figure 13. Separation performance of an 80 cm length PAMAM composite membrane with CTS in a separation experiment continuously running for 1000 h [18].
4. Conclusions
The effect of CTS/PAA polymer DN on CO₂ separation properties of membrane were studied. The membrane module with the gutter layer of CTS/PAA=1/2 DN exhibits high CO₂ separation performance under elevated pressurized conditions. The reason is CTS/PAA DN could enhance the water sorption and mechanical strength compared to CTS. The PAMAM-based composite membrane module with CTS/PAA polymer double network shows a potential for CO₂ separation from high pressure such as IGCC practical use and it will be discussed in the following paper.

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