PVA-g-PAA 가지형 공중합체 기반 촉진수송 분리막

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Facilitated Transport Membranes Based on PVA-g-PAA Graft Copolymer

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요   약: 화석 연료를 사용할 때, 불완전 연소는 필연적으로 발생하는 문제이다. 이러한 관점에서 연소 후 기체 분리는 불완전 연소 기체의 재활용 가능성을 시사한다. 이와 관련하여 본 연구에서는 일산화탄소 기체 분리용 촉진수송 고분자 분리막을 제조하였다. 이를 위해 poly(vinyl alcohol) (PVA) 주사슬 기반으로 acrylic acid (AA) 단량체를 자유 라디칼 중합법으로 PVA-g-PAA 공중합체를 제조하였다. 본 공중합체를 일산화탄소 활용에 적용하는 사례는 처음이며, 제조한 공중합체는 AgBF$_4$ 염과 HBF$_4$를 혼합하여 기체 분리막에 적용하였다. 공중합체 합성 결과는 FT-IR을 통해 분석하였으며, 공중합체와 AgBF$_4$, HBF$_4$의 상호작용은 TEM를 통해 분석하였다. 염의 첨가를 통해 일산화탄소 기체의 촉진수송 채널을 형성하였으며 이를 통해 일산화탄소 분리막 분야에 촉진수송 및 그래프팅 방법이라는 새로운 접근법을 제시하였다.

Abstract: It is inevitable to generate incomplete combustion gases when mankind utilizes fossil fuels. From this point of view, gas separation process of combustion gas suggests the possibility of recycling CO gas. In this study, we fabricated a facilitated transport polymeric composite membrane for CO separation using AgBF$_4$ and HBF$_4$. The copolymer was synthesized *via* free-radical polymerization of poly(vinyl alcohol) (PVA) as a main chain and acrylic acid (AA) monomer as a side chain. The polymer synthesis was confirmed by FT-IR and the interactions of graft copolymer with AgBF$_4$, and HBF$_4$ were characterized by TEM. PVA-g-PAA graft copolymer membranes showed good channels for facilitated CO transport. In this perspective, we suggest the novel approach in CO separation membrane area via combination of grafting and facilitated transport.

Keywords: *facilitated transport, free-radical polymerization, grafting, gas separation membrane, carbon monoxide*

1. Introduction

Fossil fuels has been utilized as main energy sources for mankind for several decades[1-3]. However, several incomplete combustion gases are generated from the fossil fuels such as carbon monoxide (CO)[4-6]. CO has one more opportunity to be utilized as an energy source in the incomplete combustion[7]. Therefore, we can not

only prevent to emit the toxic gas but also generate extra energy. Before using CO gas, one problem still remains; CO should be separated from gases mixtures. Gas separation has been widely conducted *via* several approaches in the industry such as distillation and adsorption[8-10]. One of the efficient ways to separate CO from incomplete combustion gases is to apply gas separation membranes, which consumes small amounts of

energy[11-14].

There are promising candidates for gas separation membranes such as metal oxides and organics[15-17]. Polymers has been widely studied as the gas separation membrane due to facile processability and good economic aspects[18-20]. For example, Yave *et al.* reported CO_2/N_2 separation membrane with CO_2-philic block copolymer, poly(ethylene oxide)-poly(butylene terephthalate) [21]. Ethylene oxide and terephthalate functional group have good interactions with CO_2 gas so that the copolymer enhanced the solubility of CO_2. Another study was conducted by Ho *et al.* for separation membranes of olefin/paraffin gas using Ag^+-containing polymer[22]. Ag^+ ion have selective interactions with an olefin gas as a carrier, which has a pi-bond in the molecule. However, polymeric separation membranes for CO/CO_2 or CO/N_2 mixtures have been rarely studied in the Ag^+ ion containing membranes[23].

In the gas separation membrane area based on polymer matrix, three kinds of gas separation mechanism have been applied; i.e. molecular sieve, solution-diffusion and facilitated transport. Molecular sieve is the mechanism to separate gases via the pore size of membranes[24] and solution-diffusion mechanism utilizes two variables such as solubility and diffusivity parameters through the polymer matrix. The solubility is largely dominated by the interaction between the polymer matrix and gas molecules while the diffusivity is done by the free volume among polymer chains or porous fillers[25]. Facilitated transport employs the gas carrier to transport the target gas[26]. That is, the target gas hops among the fixed carrier by the interaction between the gas and the carrier. In this study, fixed Ag(I) gas carrier preferably interacts with CO gas because the pi-bond density of CO gas is higher than that of CO_2 gas. In addition, we investigated the effect of HBF_4 on Ag(I) ion because H^+ in HBF_4 can prevent a reduction behavior of Ag^+ ion to Ag metal[27].

In this study, we synthesized poly(vinyl alcohol)-*g*-poly(acrylic acid) (PVA-*g*-PAA) graft copolymer via free-radical polymerization and utilized as the matrix for the facilitated transport membranes for CO separation.

The synthesis of PVA-*g*-PAA was confirmed by Fourier-transformed Infrared (FT-IR) spectroscopy and the interactions among the components were analyzed by high-resolution transmission electron microscopy (HR-TEM). The structure of fabricated composite membranes were observed by field emission scanning electron microscope (FE-SEM).

2. Experimental Section

2.1. Materials

PVA (M_w 85,000~124,000, 99+% hydrolyzed), acrylic acid (AA, anhydrous, contains 200 ppm MEHQ as inhibitor, 99%) and ammonium cerium(IV) nitrate (CAN, ACS reagent, ≥ 98.5%) catalyst were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO), ethyl acetate and n-hexane were purchased from Duksan Industry (South Korea). The porous polysulfone support was supported by Toray Co. (South Korea).

2.2. Polymerization of PVA−*g*-PAA graft copolymer

PVA-*g*-PAA graft copolymer was synthesized *via* free-radical polymerization using CAN as the initiator [28]. First, 6 g of PVA was dissolved in 95 mL of DMSO in a round-bottom flask at 60°C and 0.25 g of CAN was dissolved in 5 mL of DMSO. At the same time, acrylic acid was filtered in the column to remove the MEHQ inhibitor. After the homogeneous dissolution, 18 g of acrylic acid (AA) was added in the PVA solution. The PVA/AA solution was purged by nitrogen gas after sealing with a rubber septum. Then, the CAN solution was added to the PVA/AA solution by a syringe during N_2 purging. The solution was reacted for 20 hours at 60°C. After the reaction, the polymer solution was precipitated and washed in the mixture of ethyl acetate/n-hexane (1 : 1 by volume ratio). The resultant polymer was then dried at 50°C overnight.

2.3. Fabrication of membranes

The polysulfone support was prepared for washing and O_2 plasma process. The support was washed in ethanol for 2 hours and dried overnight. Also, the support was

Table 1. Content of Materials used for the Preparation of Membranes

| Membranes	Polymer [g]	$AgBF_4$ [g]	HBF_4 [g]	Solvent
PVA-g-PAA/Ag 75%		0.45	0.09	
PVA-g-PAA/Ag 77.5%	0.15	0.50	0.10	6 mL of H_2O/EtOH 1 : 1 mixture
PVA-g-PAA/Ag 80%		0.60	0.12	
PVA-ggPAA/Ag 82.5%		0.71	0.14	

treated by O_2 plasma for 30 sec. The amounts of materials used in this study were shown in Table 1. 0.15 g of PVA-g-PAA graft copolymer was dissolved in 6 mL of mixed solvent at 60°C. After the homogeneous dissolution, the various amounts of $AgBF_4$ and HBF_4 were added to the solution and stirred for 4 hours. The resultant solutions were coated onto the O_2 plasma-treated polysulfone substrate by RK coater (Model 101, Control RK Print-Coat Instruments Ltd., UK) and dried overnight.

2.4. Characterization

The functional groups of PVA-g-PAA graft copolymers were characterized by FT-IR spectra (Spectrum 100, PerkinElmer, USA) from the range of 4,000~500 cm^{-1} wavenumber. The structures and morphology of membranes were characterized by TEM (JEM-F200, JEOL, Japan). The cross-sectional images of fabricated membranes were observed by FE-SEM (AURIGA, Zeiss, Germany).

2.5. Gas separation properties

Gas permeation measurements were carried out using a constant pressure/variable volume apparatus purchased from Airrane Co., Ltd. (Korea) with the active area of 10.2 cm^2[29,30]. The gas permeance was determined by monitoring the flow rate of the permeated gas and the pressure difference between the permeate and retentate regions of the membrane chamber. The selectivity of the membrane was obtained by dividing the permeance data of each gas. Here, we note that the unit of gas permeance is GPU, where 1 GPU = 10^{-6} cm^3 (STP)/(s · cm^2 · cm Hg).
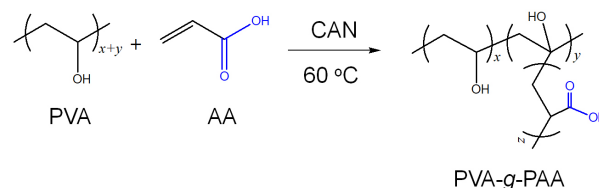
Fig. 1. Synthetic route of PVA-g-PAA graft copolymer *via* free-radical polymerization.

3. Result and Discussion

The polymerization process of PVA-g-PAA graft copolymer (PVA-g-PAA) *via* CAN as the initiator was described in Fig. 1. PVA was selected as a main chain of gas separation membrane in this study. It contains hydroxyl functional groups (-OH), which results in the high solubility in water and good miscibility with ionic salts. That is, it refers to the high dissociation of ionic salts. Therefore, it was expected that PVA could act as the promising matrix of gas separation membranes for facilitated transport system. Acrylic acid (AA), which is a side chain in this study, could minimize the solubility parameter of CO_2 gas, resulting in lower CO_2 permeance and high CO/CO_2 selectivity.

The polymerization of PVA-g-PAA was confirmed by FT-IR spectra by comparing with neat PVA and AA monomer (Fig. 2). The hydroxyl functional group is a main characterization absorption band in PVA, which was shown at 3,273 cm^{-1}. When AA was attached onto the PVA main chain, the band was shifted higher wavenumber to 3,340 cm^{-1}. The band shift resulted from the strengthen bond energy by steric hindrance when AA was attached on the main chain. The characteristic absorption band of AA (C=O double bond at 1,697 cm^{-1}) was also observed in the graft copolymer. In addition,
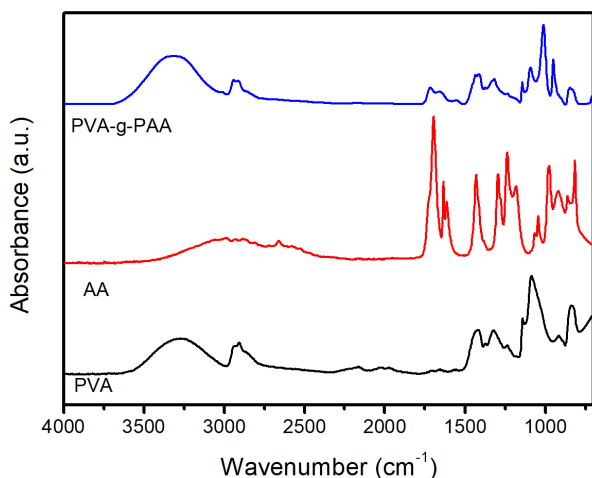
Fig. 2. FT-IR spectra of PVA, AA monomer and synthesized PVA-*g*-PAA graft copolymer.
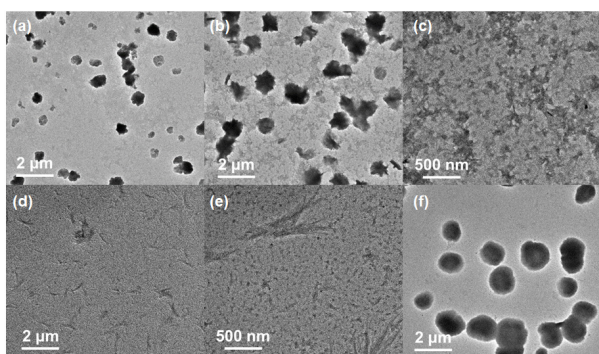

Fig. 3. TEM images of (a) PVA-*g*-PAA/Ag75, (b, c) PVA-*g*-PAA/Ag80, (d, e) PVA-*g*-PAA/Ag80 without HBF₄ and (f) PVA-*g*-PAA/Ag85.

the C=C double bond at 1,625 cm^{-1} completely disappeared in the spectrum of graft copolymer, which proves the washed unreacted remainder. Therefore, we concluded that the polymerization of PVA-*g*-PAA graft copolymer was successful by free-radical polymerization.

The chain behaviors and nanostructures of graft copolymer and membranes were investigated by TEM (Fig. 3). The dark dots referred to the PAA side chains and bright region represents the PVA main chains. The effect of HBF₄ in the materials was also investigated in this section. When HBF₄ was added in PVA-*g*-PAA/AgBF₄ mixture, micron-size clusters are formed (Fig. 3a, b, f). However, PVA-*g*-PAA/Ag75 and PVA-*g*-PAA/Ag85 did not show any interconnectivity among mi-
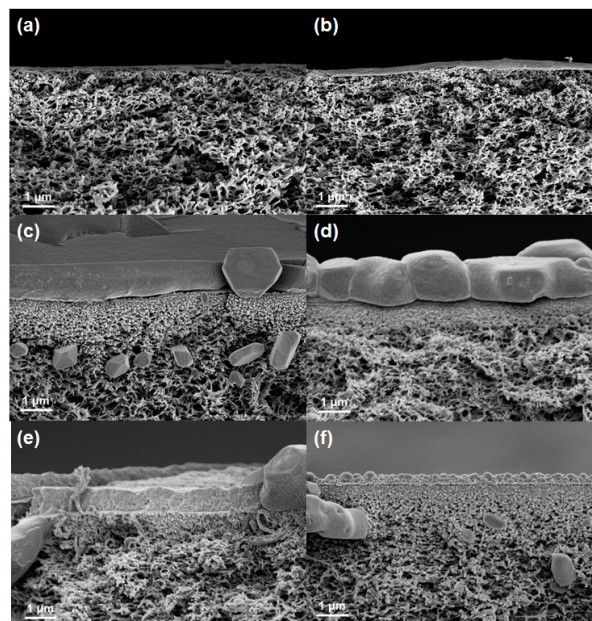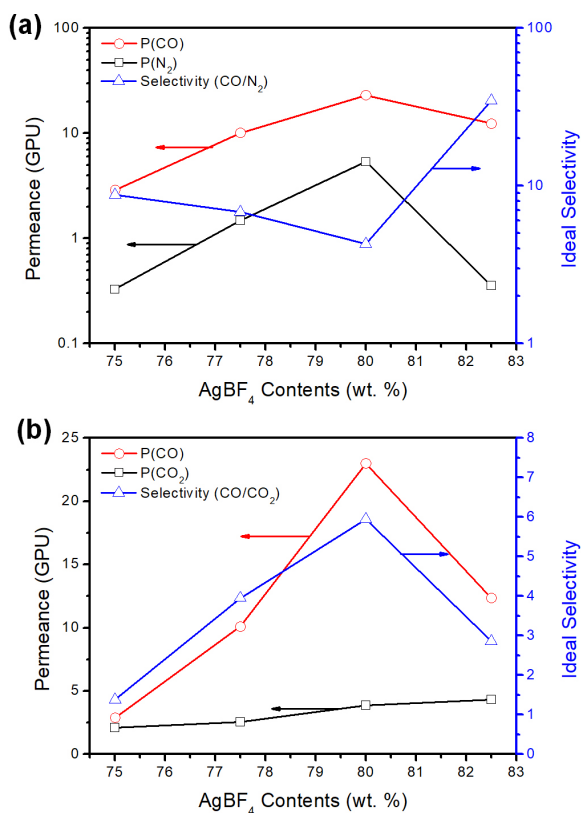

Fig. 4. Cross-sectional FE-SEM images of (a) neat polysulfone support, (b) O₂ plasma-treated PTMSP gutter layer on polysulfone support, (c) PVA-*g*-PAA/PTMSP on polysulfone support, (d) PVA-*g*-PAA/Ag75 on polysulfone support, (e) PVA-*g*-PAA/Ag80 and (f) PVA-*g*-PAA /Ag85 on polysulfone supports.

cron-clusters unlike interconnected PVA-*g*-PAA/Ag80 (Fig. 3b, c). The PVA-*g*-PAA/Ag salt without HBF₄ showed smaller scale of nanostructure (Fig. 3d, e) as Ag(I) salt was distributed homogeneously throughout the polymer matrix. The PVA-*g*-PAA/Ag80 was considered to be the most adequate system to apply to facilitated transport mechanism *via* fixed Ag(I) carrier.

The cross-sectional images of fabricated composite membranes on the porous polysulfone support were observed by FE-SEM (Fig. 4). The neat polysulfone support did not show any dense selective layer (Fig. 4a). Upon coating of PTMSP gutter layer with O₂ plasma treatment, a thin selective layer was observed in Fig. 4b. The PVA-*g*-PAA neat membrane exhibited the clear cross-section with 1 μm-thickness (Fig. 4c) while the PVA-*g*-PAA/Ag75 membrane exhibited a 1.3 μm thick dense layer in the cross-section (Fig. 4d). The optimum thickness (760 nm) without Ag reduction could be obtained in PVA-*g*-PAA/Ag80. However, the excess amount of Ag salt resulted in the reduction to Ag along with
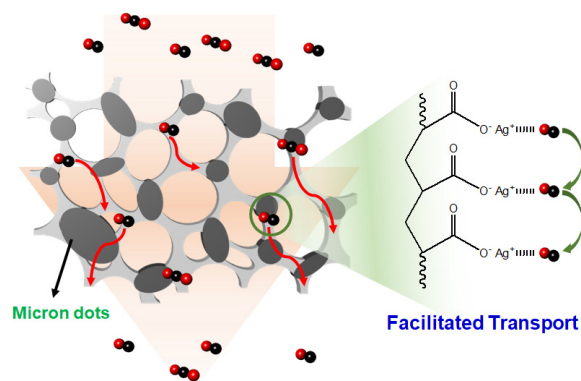
Table 2. CO/N$_2$ and CO/CO$_2$ Gas Separation Performance of Membranes based on PVA-*g*-PAA Graft Copolymer

	P(N$_2$) [GPU]	P(CO$_2$) [GPU]	P(CO) [GPU]	α (CO/N$_2$)	α (CO/CO$_2$)
Neat PVA			Not detected		
PVA-*g*-PAA	2.07	1.41	2.0	1.0	1.4
PVA/Ag80	0.43	1.06	1.6	3.8	1.5
PVA-*g*-PAA/Ag75	0.33	2.09	2.9	8.8	1.4
PVA-*g*-PAA/Ag77.5	1.48	2.55	10.1	6.8	4.0
PVA-*g*-PAA/Ag80	5.36	3.87	23.0	4.3	6.0
PVA-*g*-PAA/Ag82.5	0.36	4.32	12.3	34	3.0

Fig. 6. Schematic illustration for the structure and mechanism of PVA-*g*-PAA/AgBF$_4$ facilitated CO transport membranes.

Fig. 5. CO/N$_2$ and CO/CO$_2$ gas separation performance of PVA-*g*-PAA membranes with different AgBF$_4$ contents. All membranes contain HBF$_4$ stabilizer.

partial penetration into the pores of polysulfone support. To summarize, it is supported that PVA-*g*-PAA/Ag80 will show the best gas separation performance.

Gas separation performances are shown in Fig. 5 and Table 2. Nitrogen gas permeance represents the diffusivity of gas through the membrane. Therefore, we can infer that the permeance difference between CO or CO$_2$

and N$_2$ indicates the enhancement by facilitated transport. PVA was known to be a gas barrier so that gas permeation through neat PVA was not detected even in the thin film composite membranes. The PVA-*g*-PAA graft copolymer membrane showed increased permeances of all gases due to the decreased crystallinity of PVA main chains and increased free volume of membrane. However, the PVA-*g*-PAA graft copolymer without Ag salt was not selective to separate CO from N$_2$ or CO$_2$.

The effect of AgBF$_4$ salt contents was investigated by changing the loading amounts. The structure and mechanism of PVA-*g*-PAA/AgBF$_4$ facilitated CO transport membranes are shown in Fig. 6. The ionized Ag ion (Ag$^+$) acted as the CO carrier and thus enhanced the permeance of CO as well as the selectivies of CO/CO$_2$ and CO/N$_2$, resulting in the facilitated CO transport. The increasing trend of gas permeance and selectivies continued until the contents of AgBF$_4$ reached to 80

wt.% in the membrane. The excessive amount of $AgBF_4$ salt, i.e. 82.5 wt.%, was not sufficiently ionized and thus formed highly ionic aggregates. The non-dissolved $AgBF_4$ salt reduced gas permeating path through the membranes and reduced diffusivity. Moreover, the suppression effect of acrylic acid for CO_2 transport was reduced due to too low contents of PVA-*g*-PAA graft copolymer matrix and thus the CO/CO_2 selectivity was decreased.

4. Conclusion

In this study, we synthesized PVA-*g*-PAA graft copolymer for the matrix of facilitated CO transport membranes. Free-radical polymerization was applied onto the PVA main chain with AA monomer using CAN initiator. Ag(I) ion is a core source for facilitated CO transport in the composite membrane with HBF_4 stabilizer. The PVA-*g*-PAA/$AgBF_4$ was coated onto the O_2-plasma-treated porous polysulfone support to form thin film composite membranes. PAA side chains selectively blocked the acidic CO_2 gas while Ag(I) ion selectively interacted with CO gas as the facilitated transport carrier. As a result, the PVA-*g*-PAA/Ag80 membrane exhibited 23.0 GPU of CO permeance, 4.3 of CO/N_2 selectivity and 6.0 of CO/CO_2 selectivity, which represents good separation performances for CO from CO_2 or N_2 gases.

Acknowledgements

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