

## 기체 분리용 탄소분자체 막의 제조방법 및 특성평가

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### Preparation and Characterization of Carbon Molecular Sieve Membranes for Gas Separation

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#### 1. Introduction

Since carbon molecular sieve (CMS) membrane materials appeared as gas separation membranes, their excellent gas separation performance has been demonstrated in a number of works [1]. In the CMS membranes, the physical properties of microporous carbon materials and their gas separation properties mainly depend upon the pyrolysis conditions, such as pyrolysis temperature, heating rate, isothermal times, and pyrolysis atmospheres [2, 3].

Until now, many researches have been focused on the definition of gas separation properties of CMS membranes derived from some polymer precursors, such as polyimide, phenolic resin, and polyfurfuryl alcohol and studied the effect of pyrolysis conditions on the properties of microporous carbon structures. In previous studies [4], we have prepared novel pyrolytic carbon-silica membranes using poly(imide siloxane) and varied the difference structures as compared to CMS membranes derived from polymeric precursors through the pyrolyzed products.

In the present study, we have investigated the roles of chemical structures of aromatic polyimides and the effect of micro-phase separation domain on the properties of microporous carbon structures. In addition, high permeable and selective carbon molecular sieve membrane materials were prepared using polymer-blending method.

## 2. Experimental

Polyimide was synthesized using dianhydride and diamine monomers. The dianhydride monomers were benzophenone tetracarboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA), and the diamine monomers were 4,4'-oxydianiline (ODA), 1,3-phenylene diamine (mPDA), 2,4-diaminotoluene (2,4-DAT), 2,4,6-trimethyl-1,3-phenylenediamine (m-TMPD), 1,3-diamino benzoic acid (DBA), and  $\alpha,\omega$ -aminopropyl polydimethylsiloxane (PDMS). Polyvinylpyrrolidones (PVP,  $M_w$  10,000, 40,000, and 55,000) were used as a thermally labile polymer additive.

## 3. Results and Discussion

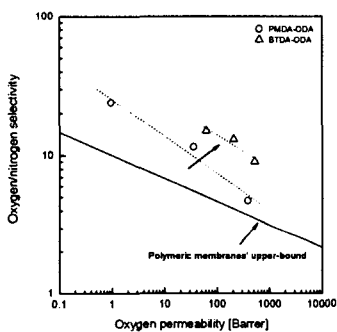


Fig. 1

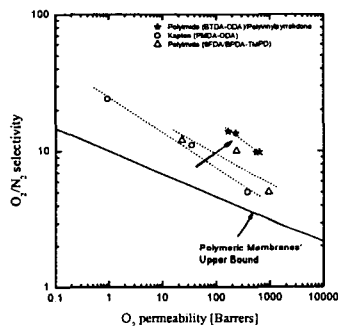


Fig. 2

Fig. 1. shows the  $O_2$  permeabilities vs  $O_2/N_2$  selectivities of the CMS membranes derived from PMDA-ODA and BTDA-ODA polyimides. In polyimide membranes, PMDA-ODA polyimide showed higher gas permeability than BTDA-ODA polyimide due to high fractional free volume even though PMDA-ODA polyimide has rigid structural characteristics. On the other hand, the CMS membranes derived from BTDA-ODA polyimide showed the improved permeabilities and selectivities. That is, the properties of microporous carbon structures are very closely related to the thermally evolvable groups, such as ketone (-CO-) bridge groups or pendant side groups (-CH<sub>3</sub>, -COOH, and SO<sub>3</sub>H).

Fig. 2 shows the  $O_2$  permeabilities and  $O_2/N_2$  selectivities of the CMS membranes prepared using a polymer-blending method. In general, the microporous carbon structures were essentially controlled by the pyrolysis

conditions and the chemical structures of polymer precursors. However, polymer blends consisted of micro-phase separation domains formed from two polymers showed the alternating polymer precursors on the controlling microstructures (pore volume and pore size) of CMS membranes having high permeation properties. As shown in Fig. 2, the CMS membranes using pyrolyzed polymer blend precursors showed the improved permeation performances as compared to the CMS membranes derived from polyimides.

#### 4. Conclusions

To separate small gas molecules, such as He/N<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub>, and CO<sub>2</sub>/CH<sub>4</sub>, the CMS membranes might obtain the micro-pores. In this study, the micro-structures of the CMS membranes were controlled by the tuned polyimide structures as well as the pyrolysis conditions. Also, the micro-phase separation domains of the thermally labile polymers acted as a pore forming agent in the micro-porous CMS membranes in the range of micro-pores and significantly improved their gas permeation performances.

#### Acknowledgement

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#### References

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