

**폴리이미드 전구체의 화학적 구조에 따른 탄소분자체막의
수증기흡착거동 및 기체 투과 특성**

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**Water vapor sorption behavior and gas permeation
properties of carbon molecular sieve membranes
derived from polyimides with different chemical
structures**

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1. Introduction

The molecular sieve carbon membrane in the application of gas separation have attracted more attention in recent years and is now rapidly developing. This is due to their excellent characteristics for gas separation as compared with conventional polymeric membranes [1]. Koresh and Soffer [2] first formed a carbon molecular sieve membranes (CMSM). Since then, carbonized membranes have been prepared from polyfurfuryl alcohol resin [3], poly(vinylidene chloride) resin [4], phenol formaldehyde resin [5] and polyimides [6]. Carbonization of polyimides has been most intensively investigated [7, 8]. Hayashi et al. [9] coated a polyimide film made from 3,3',4,4'-biphenylcarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) on the outer surface of a porous alumina support tube and obtained a CMSM by carbonization at 600-900°C in an inert atmosphere.

The objective of this study was to prepare carbon molecular sieve membranes (CMSM) and to investigate the role of the methyl(-CH₃) pendent groups in the polyimide during the pyrolysis in water vapor sorption behaviors and gas separation properties.

2. Experimental

2.1. Materials

Materials used in the synthesis of polyimide included benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydianiline (ODA), *meta*-phenylenediamine (*m*PDA), *m*-toluylenediamine (*m*TDA) and 2,4,6-trimethyl-1,3-phenylenediamine (*t*TDA). BTDA and *m*PDA were purchased from the Aldrich Chemical Co. Before polymerization, all the monomers were purified by the sublimation under reduced pressure. ODA, *m*TDA and *t*TDA were purchased from TCI Co. (Tokyo, Japan). Dimethylsulfoxide (DMSO) was used for polyimide synthesis.

2.2. Preparation polyimide precursors

Polyimide (PI) was prepared by casting the poly(amic acid) (PAA) solution on the glass plate and then thermally imidized in the vacuum oven by a four-step imidization protocol: 60°C/1hr, 150°C/1hr, and 200°C/1hr and 250°C/30min, respectively. The thickness of the PI film was approximately 40μm (See Table 1).

2.3. Pyrolysis protocol

The pyrolysis protocol used in this work is determined by the result from thermogravimetric analysis coupled with mass spectroscopy (TGA-MS). The final pyrolysis temperature was 600, 800 or 1000°C. The heating rate was slowed to 3°C/min until the temperature reached up to 600, 800 or 1000°C. Then the precursor films were kept at the final temperature for 60min. At each stage, the furnace was allowed to cool slowly to room temperature. The final pyrolytic carbon molecular sieve membranes were taken from quartz tube and then stored in a dessicator filled with dry silica gel to eliminate the humidity effect.

Table 1. Preparation polyimide precursors with the various amine monomers.

Sample codes	Pyrolysis Temp (oC)	BTDA (mmol)	ODA (mmol)	mPDA (mmol)	mTDA (mmol)	tTDA (mmol)
C600-M0	600	10	9	1		
C600-M1		10	9		1	
C600-M3		10	9			1
C800-M0	800	10	9	1		
C800-M1		10	9		1	
C800-M3		10	9			1
C1000-M0	1000	10	9	1		
C1000-M1		10	9		1	
C1000-M3		10	9			1

3. Results and Discussion

The TGA spectrum of the polyimide showed approximately 5% weight loss in a 300-400°C temperature interval due to the removal of methyl groups. The water vapor sorption behavior of the CMSMs that were pyrolyzed at 600, 800 and 1000°C were investigated at 25°C and 60% RH. The water uptake and diffusion coefficient were showed in Figure 1 and 2. The diffusion coefficient was calculated by Eq. (1). From the results, the water uptake and diffusion coefficient of CMSMs that was pyrolyzed at 800°C was showed highest. The water vapor sorption behaviors of the CMSMs may be affected by the interplannar distance of carbon structures.

$$D = \frac{\pi}{16} \left[\frac{d(M_t/M_\infty)}{d(\sqrt{t/l})} \right]^2 \quad (1)$$

The structure of CMSMs were controlled with the pyrolysis temperatures and the structure of precursors with the bulky pendent groups.

Gas permeabilities were measured at 25°C with a high-vacuum (<10⁵torr) time-lag method under the pressure difference of 200torr. The gas permeabilities of the selected gases were shown to be in the order of He>CO₂>O₂>N₂. In case of C600-M3 showed the permeability of 200

Barrer for O_2 and the selectivity of 10 for O_2/N_2 .

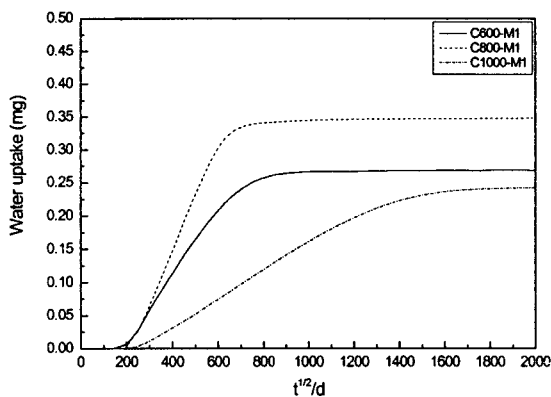


Figure 1. Water uptake of CMSM-M1

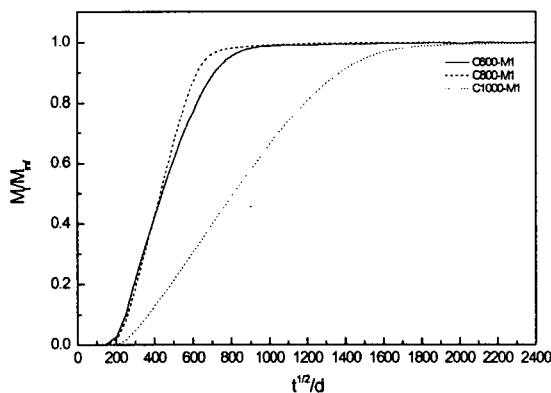


Figure 2. Water vapor sorption behavior of CMSM-M1

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