

## 열분해성 고분자 도입에 따른 탄소분자체막의 기체 투과 특성

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### Carbon Molecular Sieve Membranes Derived from Thermally Labile Polymer Containing Polyimides and Their Gas Separation Properties

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#### 1. Introduction

Gas separation membranes are now used in a wide variety of application areas as oxygen enrichment, hydrogen recovery, acid gas treatment, and natural gas dehydration etc [1]. Since polymeric membranes offer attractive properties for gas separation application, they have been variously studied [2-4]. However, current polymeric membrane materials have apparently shown a limit in the productivity-selectivity trade-off. To solve this limitation, much research is focused on nano-porous molecular sieving materials such as carbon molecular sieve (CMS), silica and zeolites. Carbon molecular sieve (CMS) membranes are revealed they offer excellent permeabilities and selectivities [5]. In this study, we prepared CMS membranes derived from PI/PVP blend polymers pyrolyzed by different final pyrolysis temperatures and different molecular weight of PVP, and investigated the structural characteristics of CMS membranes. Furthermore, the effect of pyrolysis temperatures and molecular weight of PVP focused on the gas permeation properties of CMS membranes using small gas molecules [He (2.6 Å), CO<sub>2</sub> (3.3 Å), O<sub>2</sub> (3.46 Å) and N<sub>2</sub> (3.64 Å)]

## 2. Experimental

For the preparation of PI/PVP blend polymers, thermal imidization was performed. In a moisture free three-neck flask with nitrogen inlet and magnetic stirrer, ODA was dissolved in DMSO for 3 h and then the powder of BTDA was added gradually at room temperature. The reaction mixture of 20 wt% was then stirred for 3 h at room temperature to yield a high molecular poly(amic acid) (PAA) solution. To prepare the PAA/PVP blend polymer solutions, 5 wt% PVP (M.W 10,000, 40,000, and 55,000) was added to PAA solution, respectively. The preparation procedure of PI/PVP blend polymers and CMS membranes is illustrated in Fig. 1. For the preparation of PI/PVP blend polymers, PAA solutions were thermally imidized in a vacuum oven using the four-step imidization protocol: 50 °C for 3 h, 100 °C for 1 h, 200 °C for 1 h and 250 °C for 30 min. To take off the PI/PVP blend polymer membranes from the glass plate, the glass plate should not be dipped into deionized water because PVP is soluble in water.

Finally, CMS membranes were prepared by pyrolysis of their PI/PVP blend polymers at different final pyrolysis temperatures (550 and 700 °C). PI/PVP blend polymer was placed in the middle of a quartz tube and pyrolyzed under flowing argon gas (flow rate = 300 cm<sup>3</sup> (STP)/min) in a tube furnace supported on an alumina holder plate.

## 3. Results and Discussion

In TGA thermograms of PI/PVP blend polymers (PI-P10, PI-P40, and PI-P55), the first weight loss observed in the range of 400-450 °C, and the second weight loss began at about 550 °C. That is, the first weight loss is appeared due to the decomposition of PVP, and the second weight loss is observed caused by decomposition of PI. These different thermal decomposition behaviors predict the different carbon structures of final CMS membranes after pyrolysis because of different molecular weight (chain length) of PVP. These phenomena will be explained reasonably through the gas permeation properties of CMS membranes.

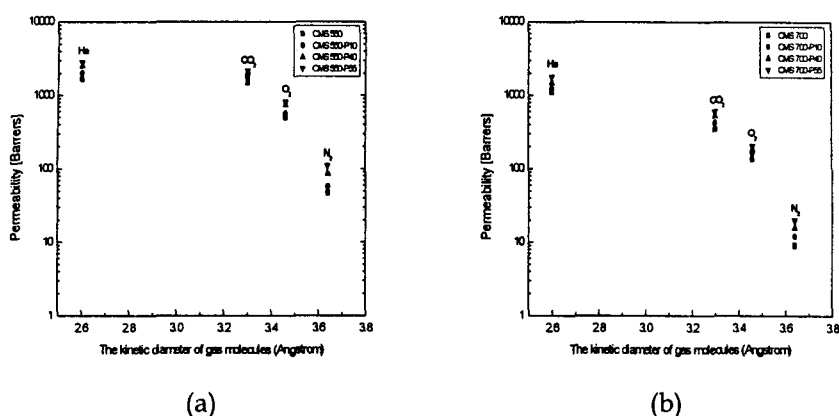


Fig. 1 Gas permeabilities of CMS membranes pyrolyzed at (a) 550 and (b) 700 °C

Gas permeation properties of CMS membranes were reevaluated with pure single gas permeation experiments at 25 °C. In present study, the gas permeation properties of CMS membranes investigated concerning the final pyrolysis temperatures and different molecular weight of PVP (MW 10,000, 40,000, and 55,000). As shown in Fig. 1, the gas permeabilities of CMS membranes pyrolyzed at 550 and 700 °C increased with increasing the molecular weight of PVP. The gas permeation results indicated that the different molecular weight of PVP constructed different pore volume in carbon matrix caused by amounts of removed PVP during the pyrolysis.

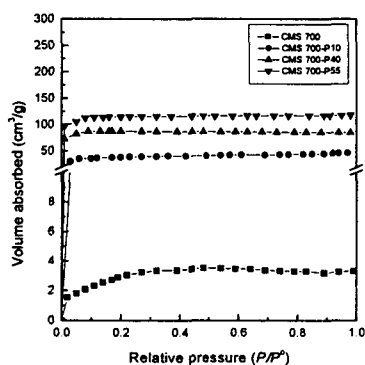


Fig. 2 N<sub>2</sub> adsorption experimental data of CMS membranes

These phenomena explained that the reasonable agreement with gas permeabilities of CMS membranes. To confirm the gas permeation results of CMS membranes derived from PI/PVP blend polymers, nitrogen gas adsorption experiment [BET (Brunauer-Emmett-Teller) method] was performed additionally as shown in Fig. 2. The nitrogen adsorption volumes for CMS membranes derived from PI/PVP blend polymers showed much higher than CMS membranes derived from polyimide. The volume of nitrogen absorbed in the CMS membranes increased in the order CMS700-P55 > CMS700-P40 > CMS700-P10 >> CMS700. These results surely showed that the pore volume in carbon structures influenced by the molecular weight of PVP during the pyrolysis

#### **4. Conclusions**

The thermally labile polymers mainly affected the pore volume in carbon matrix during the pyrolysis, which provided the more diffusional path-way to transport of gas molecules. In addition, the different molecular weight (chain length) of PVP constructed the different porous carbon structures during the pyrolysis. By the final pyrolysis temperature, the gas permeabilities and selectivities of CMS membranes mainly depend on the pyrolysis temperatures. In this study, CMS membranes pyrolyzed at 700 °C showed that the decreased gas permeabilities and increased selectivities due to the constructed pore volume or pore size reduced by the higher pyrolysis temperature.

#### **References**

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