

## 열분해 온도에 따른 PPO 탄소막의 기체투과 특성의 영향

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## Gas Permeation Properties of Carbon Membranes Derived from PPO (Polyphenylene Oxide): Effect of the Pyrolysis Temperature

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### 1 Introduction

Attractive opportunities for gas separation using inorganic membranes are found in the various application areas because of thermal and chemical stability [1]. Of inorganic membranes, carbon molecular sieving (CMS) membrane is considered to be one of the promising materials for membrane-based gas separation because of their excellent permeation and separation properties and thermal and chemical stability even under harsh conditions, such as high pressure and high temperature [2,3]. The preparation of carbon membranes having high permeation performances involves the following several steps: polymeric membrane preparation using polymeric precursors, pre-treatment, pyrolysis/carbonization and post-treatment as an additional step [4]. Among polymeric precursors, PPO (polyphenylene oxide) is considered as one of the alternative promising polymeric materials for carbon membrane preparation because of a high glass transition temperature [5]. In addition, PPO polymer membranes have a somewhat high gas permeability among aromatic polymeric membranes since the presence of ether linkages and the absence of polar groups inhibit chain packing and densification [6]. Furthermore, the methyl groups attached on both sides of phenyl ring hinder the free rotation of the phenyl ring, resulting in the moderate selectivity in the PPO membranes

[7]. It was reported that the correlation of the permeability and the selectivity for PPO polymer membranes approaches the Robeson line, the upper bound line for polymer membranes [8].

Until now, the preparation of carbon membrane derived PPO polymer and the permeation results have been rarely reported. In this study, the carbon membranes derived from PPO polymer were prepared by the consecutive steps, such as polymeric membrane preparation, pre-treatment, and pyrolysis. The influence of the different pyrolysis temperature on the permeation performances was investigated for the PPO derived carbon membranes. And, the pore properties were characterized in order to investigate the influence of different pyrolysis temperature on the pore structures.

## 2 Experimental

Using 3 wt% PPO polymer (#18,178-1, Aldrich, USA) in  $\text{CHCl}_3$  (Wako, Japan), the carbon membranes were prepared by the preoxidation of the coated PPO polymer on a macroporous tubular ceramic support (pore size: 100 nm and porosity: 41 %) in the stagnant air condition, followed by the pyrolysis. The carbonization was performed by heating up to the maximum pyrolysis temperatures and cooling (rate of heating and cooling: 5 °C/min) in the Ar atmosphere (flow rate: 200 ml/min) [9]. The maximum pyrolysis temperatures were changed between 500 and 800 °C and the duration time of each temperature was set to 1 hour. The preparation steps (preoxidation and pyrolysis) were repeated twice for making carbon membranes without defects.

The surface morphology and cross-section of the carbon membrane were examined using a scanning electron microscope (SEM), S-900 (Hitachi, Japan). Weight change during heat treatment of PPO polymer was evaluated under Ar atmosphere (heating rate: 5 °C/min and flow rate: 200 ml/min) by means of a thermogravimetric analyzer (TG-DTA2000SA, Bruker AXS). The pore properties of pyrolyzed carbon materials were characterized by the nitrogen adsorption at 77 K using an automatic adsorption apparatus (BELSORP-18, BEL Japan, Inc.) after the pyrolyzed carbon materials were pretreated at 300 °C during 5 hours in the vacuum condition. Also, the adsorption amount of  $\text{CO}_2$  was measured for the

pyrolyzed carbon materials at 25 °C.

Gas permeance of selected gas species, He (0.26 nm), CO<sub>2</sub> (0.33 nm), N<sub>2</sub> (0.364 nm) and CH<sub>4</sub> (0.38 nm), was measured using a permeation apparatus having a film flow meter (STEC, Japan) at the permeation temperature of 150 °C. The influence of the pyrolysis temperatures on the gas permeation performances was investigated for the PPO derived carbon membranes. And the permselectivity in the gas permeation experiments was estimated as the ratio of the permeance of each gas species.

### 3 Results and discussion

In the thermal stability of the preoxidized PPO polymer, it was observed that the total weight loss was measured to 70 % during the heat treatment up to 700 °C, which is considered to be a somewhat higher value compared with the results for different polymeric precursors. In the previous results, the weight loss of the polyimide was reported to be 40 % [1] and the phenolic resin 35 % [10]. The thermal gravimetric plot shows that the polymer structure started to degrade and develop the carbonized structure at around 400 °C [11]. In the SEM analysis of the carbon membrane pyrolyzed at 700 °C, the PPO carbon layer has a dense film structure on the surface of the macroporous ceramic support. The thickness of the PPO derived carbon layer on the support was measured as 3.1±0.2 μm. Based on the nitrogen adsorption at 77 K, the adsorption isotherm represents the Type I adsorption isotherm, indicating that the carbonized material pyrolyzed at 700 °C has a microporous structure. In the pore size distribution for the carbon material, the peak diameter was estimated as 0.43 nm by the HK (Horvath and Kawazoe) method. The pore size distribution in Fig. 1 shows that there exist the pore size distribution between 0.4 and 0.45 nm as a major portion and the larger pore distribution between 0.8 and 1.0 nm as well. In the analysis result of the BET adsorption isotherm based on the nitrogen adsorption, the pore volume and the surface area for the carbonized material were estimated to be 26.82 cm<sup>3</sup>/g and 116.75 m<sup>2</sup>/g, respectively.

The CO<sub>2</sub> adsorption was measured for the carbon materials prepared at different pyrolysis temperature and the results were shown in Fig. 2. The carbon material pyrolyzed at 500 °C showed the smallest value for the CO<sub>2</sub> adsorption in

the figure. The CO<sub>2</sub> adsorption increased with increasing pyrolysis temperature between 500 and 700 °C, the carbon material pyrolyzed at 700 °C having the largest value. The result implies that the characteristic values (e.g., the pore volume and surface area) were increased during the carbonization with increasing pyrolysis temperature. In the case of the carbon materials pyrolyzed at 800 °C, the CO<sub>2</sub> adsorption amount was significantly decreased, assuming that its pore structure (pore volume and surface area) was decreased during the pyrolysis of the PPO polymer material.

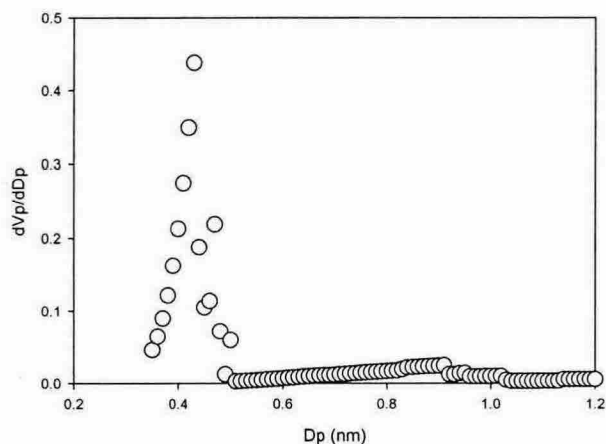


Fig. 1. Pore size distribution of the carbon material pyrolyzed at 700 °C.

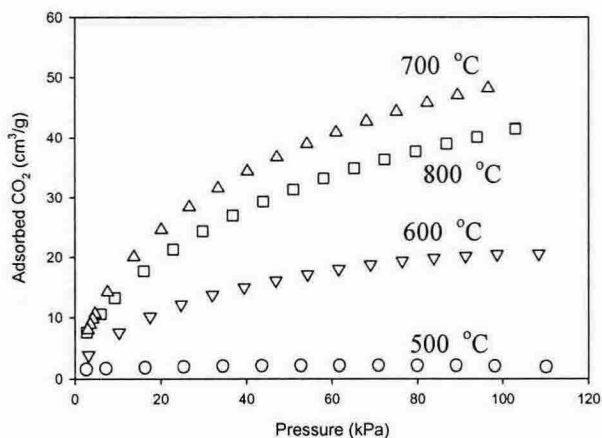


Fig. 2. CO<sub>2</sub> adsorption for the carbonized materials prepared by different pyrolysis temperatures.

Based on the CO<sub>2</sub> adsorption measurements, the characteristic values were estimated and the results were shown in Table 1. Considering the BET pore volume and surface area with different pyrolysis temperatures, the characteristic values were increased with increasing pyrolysis temperature between 500 and 700 °C. The result for the carbon material prepared at a higher temperature (800 °C) showed decreasing values. In the limiting micropore volume of adsorption using the Dubinin-Astakhov (DA) equation, the value for the carbonized material pyrolyzed at 700 °C showed the largest value as 0.238 cm<sup>3</sup>/g in Table 1. The result of the carbon material prepared at 800 °C showed a notably decreasing value (0.080 cm<sup>3</sup>/g). From the results for the CO<sub>2</sub> adsorption measurement, it is considered that the enlargement of the pore structures occurred during the carbonization with increasing pyrolysis temperature (between 500 and 700 °C). Then, the carbonization at a higher pyrolysis temperature caused the pores to shrink, decreasing the characteristic values for the pore structures for the carbon material pyrolyzed at 800 °C.

Table 1 Pore characteristic values for carbon materials based on the CO<sub>2</sub> adsorption measurements

Pyrolysis temperature	BET pore volume (cm <sup>3</sup> /g)	BET surface area (m <sup>2</sup> /g)	*Limiting micropore volume (cm <sup>3</sup> /g)
500 °C	2.08	10.90	0.004
600 °C	60.71	318.06	0.204
700 °C	78.21	409.84	0.238
800 °C	25.66	134.42	0.080

\*The value was estimated using the Dubinin-Astakhov (DA) equation (n=2).

The influences of the pyrolysis temperature on the permeation performances was investigated in the PPO carbon membranes prepared with the PPO polymer concentration of 3 wt%. Fig. 3 shows the permeation results as a function of kinetic gas diameter at the permeation temperature of 150 °C for the carbon membranes prepared with different pyrolysis temperatures. It was observed that the temperature of pyrolysis has a marked influence on permeation characteristics of the prepared carbon membranes [4]. An increase in permeance of the carbon membrane was observed as the pyrolysis temperature increased between 500 and 700 °C. However, the permeances of gas species notably decreased for the carbon

membrane pyrolyzed at 800 °C. Considering the permeance of CH<sub>4</sub> having the kinetic diameter of 0.38 nm, the value was measured to  $2.6 \times 10^{-10}$  mol/m<sup>2</sup>secPa for the carbon membrane pyrolyzed at 800 °C, about three times lower than the other carbon membranes ( $6\sim 9 \times 10^{-10}$  mol/m<sup>2</sup>secPa).

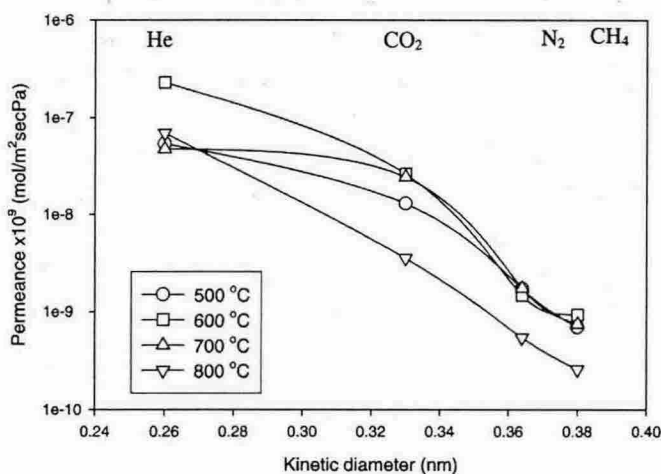


Fig. 3. Effect of pyrolysis temperature on gas permeance for the PPO derived carbon membranes.

Based on the permeation results at the permeation of 150 °C, the permeation performance of CO<sub>2</sub> was evaluated and the results were shown in Fig. 4. It was observed in Fig. 4(a) that the value of the CO<sub>2</sub> permeance was increased as the pyrolysis temperature increased up to 700 °C, then decreased for the carbon membrane pyrolyzed at 800 °C. The CO<sub>2</sub> permeance for the carbon membrane prepared at 700 °C was  $1.16 \times 10^{-7}$  mol/m<sup>2</sup>secPa, while that of the carbon membrane of 800 °C was decreased to the level of one-tenth ( $1.57 \times 10^{-8}$  mol/m<sup>2</sup>secPa). The permselectivity of CO<sub>2</sub>/CH<sub>4</sub> shown in Fig. 4(b) was increased with increasing pyrolysis temperatures (between 500 and 700 °C) and then decreased notably with a higher pyrolysis temperature (800 °C). The permselectivity for the carbon membrane pyrolyzed at 700 °C was estimated to be 33, while that of the carbon membrane prepared at 800 °C was decreased to 14. Change in gas permeation performance with pyrolysis temperature is related to the modification of the structural characteristics such as pore volume and its size distribution [12–14]. The permeation results of CO<sub>2</sub> in Fig. 4 can be explained by

change in the characteristic value for the pore structure shown in Table 1. That is, it is considered that the enlargement of the pore structure during the carbonization at the pyrolysis temperature between 500 and 700 °C increased the permeance of gas species. Decrease in the CO<sub>2</sub> permeance and the permselectivity occurred due to decrease in the pore volume at the pyrolysis temperature of 800 °C

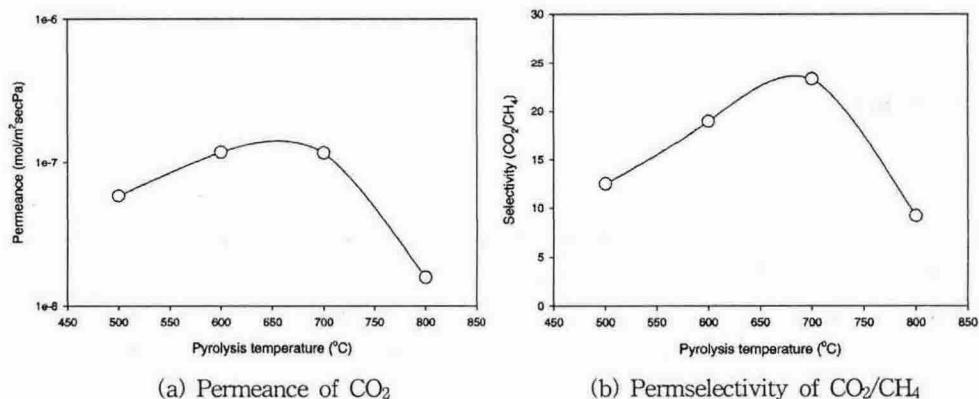


Fig. 4. Effect of pyrolysis temperature on the permeation performance of CO<sub>2</sub>.

#### 4 Conclusions

The carbon membranes were prepared by the pyrolysis of PPO (polyphenylene oxide) polymer coated on the surface of the macroporous alumina tubular ceramic support. The permeation results showed that gas transport through the PPO derived carbon membranes was controlled by the molecular sieving effect. The influence of the pyrolysis temperature on the permeation performances indicates that the pore structure developed at a low temperature and then the characteristic values (pore volume and surface area) were increased with increasing pyrolysis temperature. It is considered that the pyrolysis temperature gave a marked influence the permeation performance for the PPO derived carbon membranes.

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