

PPO/PVP 고분자 블렌드를 이용한 기체분리용 탄소막에 있어서 PVP 농도의 영향에 따른 기체 투과 성능

이홍주, Hiroyuki Suda*, Kenji Haraya*, 김동표

충남대학교 정밀공업화학과, National Institute of Advanced Industrial Science and
Technology (AIST)*

Influence of PVP Concentration on Gas Permeation Properties of Carbon Membranes Derived from the Polymer Blend of PPO/PVP

Hong-Joo Lee, Hiroyuki Suda*, Kenji Haraya*, Dong-Pyo Kim

Dept. Fine Chem. Eng. & Chemistry, Chungnam National University, National
Institute of Advanced Industrial Science and Technology (AIST)*

1 Introduction

The preparation of carbon membranes involves the following several steps: polymer precursor selection, polymeric membrane preparation, pre-treatment, pyrolysis/carbonization, post-treatment, and module construction [1]. The selection of a polymeric precursor is one of the most important considerations since it can yield a series of membranes having micropores of desired molecular dimensions through the pyrolysis at a desired temperature. Among polymeric precursors, poly(phenylene oxide) (PPO) having a high glass transition temperature is considered as one of the alternative promising polymeric materials for carbon membrane preparation [2]. It is known that carbon membrane pore structures can be modified by the post-treatment methods such as chemical vapor deposition and post-oxidation [3]. One of the methods is to carbonize polymer blend which is a physical or chemical mixture of more than two different types of polymers having different thermal properties. Since the thermally labile polymer is completely decomposed at a temperature lower than the decomposition temperature of the thermally stable polymer, the pyrolysis of blended polymer precursors will lead to

the formation of porous structure [4].

In this study, the carbon membranes derived from polymer blend of the thermally stable polymer (PPO) and the thermally labile polymer (PVP) were prepared by the consecutive steps, such as preparation of polymeric membrane on the support surface, pre-treatment, and pyrolysis of the polymeric precursor. The influences of the preparation conditions (pyrolysis temperature, blend ratio of PPO/PVP and molecular weights of PVP) on the permeation performances were investigated and the results were compared with those of the carbon membrane derived from PPO.

2 Experimental

The PPO polymer (#18,178-1, Aldrich Chemical Co., USA) was used as received as a thermally stable polymer. As a thermally labile polymer, concentrations of PVP having a molecular weight of 40 K (Aldrich Chemical Co., USA) were varied between 0.5 wt% and 1.5 wt% in the PPO/PVP blend (total concentration: 3.0 wt%) in chloroform. The carbon membranes were prepared on the surface of a tubular macroporous ceramic support (NOK, Japan). Gas permeance of each selected gas species, He (2.6 Å), CO₂ (3.3 Å), N₂ (3.64 Å) and CH₄ (3.8 Å) and C₂H₆ (4.0 Å), was measured using a permeation apparatus having a film flow meter (STEC, Japan) at the permeation temperature of 150 °C. The influences of the PVP concentration in the polymer blend of PPO/PVP on the gas permeation performances was investigated and the results were compared with those of the PPO derived carbon membrane.

3 Results and discussion

The measurement of adsorption isotherm and the determination of pore size distribution are of importance for the preparation, characterization, and gas permeation performances. Based on the nitrogen adsorption, the representative pore diameter of the carbon material derived from PPO was estimated to 0.43 nm by the HK (Horvath and Kawazoe) method in the pore size distribution. The CO₂ adsorption was measured for the carbon materials of PPO and PPO/PVP.

Considering the BET pore volume and surface area for the carbon materials prepared by the PPO/PVP blends, the characteristic values decreased compared with the carbon material of PPO. Also, the limiting micropore volume of adsorption was estimated using the Dubinin-Astakhov (DA) equation and its value of PPO carbon material was $0.242 \text{ cm}^3/\text{g}$. It was observed that the addition of PVP decreased the limiting micropore volume. It is considered in the results for the CO_2 adsorption measurements that the addition of the thermal labile polymer decreased pore volume and surface area.

Gas permeation properties of carbon membranes prepared by the pyrolysis at $700 \text{ }^\circ\text{C}$ were evaluated using single gas permeation experiments at the permeation temperature of $150 \text{ }^\circ\text{C}$. The permeance of gas species for the carbon membranes derived from PPO/PVP blends with different PVP concentration and the results were compared with those of the PPO derived carbon membrane pyrolyzed at $700 \text{ }^\circ\text{C}$ (See Fig. 1). The permeation results of all the carbon membranes show that the gas transport was controlled by the molecular sieving mechanism except for the carbon membranes prepared by high PVP concentration (0.9 and 1.5 wt%).

Considering the gas permeance increase for the carbon membranes with different PVP concentration, the He permeance showed relatively similar values for examined PVP concentrations. The permeation results showed decreased permeances for the carbon membranes prepared by the PVP concentration of 0.6 wt% or lower. The permeation results imply that the addition of PVP with low concentrations moved to the pore size distribution to a lower value and decreased pore volume. In the case of the addition of PVP with high concentrations, however, the permeances especially for gas species having large molecular size (e.g., N_2 , CH_4 and C_2H_6) notably increased compared with the PPO derived carbon membrane. It is interesting that the permeance increased for the carbon membranes with higher PVP concentration even though the pore characteristic values decreased by the addition of PVP. It is assumed that the carbon membrane prepared with high PVP concentration provided an enhanced diffusional pathway for the gas species [5].

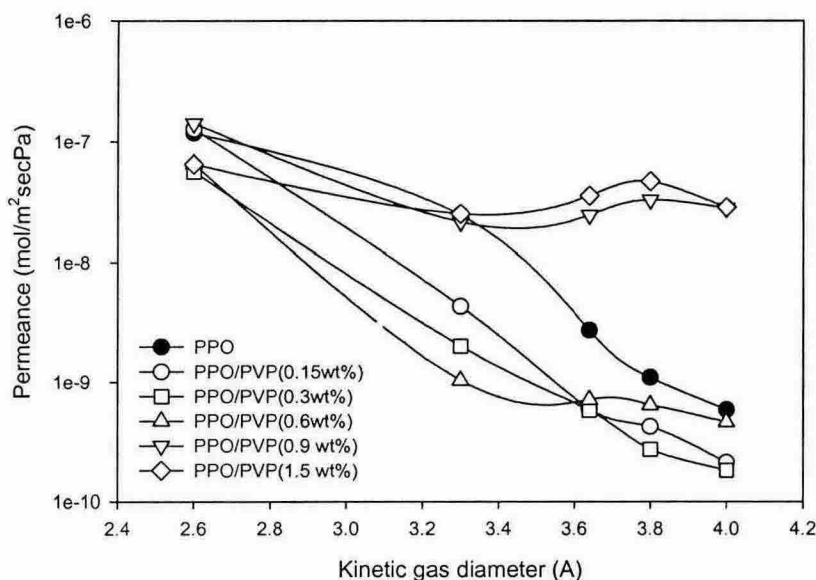


Fig. 1. Gas permeance for the carbon membranes with different PVP concentrations.

4. Conclusions

The carbon membranes derived PPO/PVP precursors were prepared using a polymer blend of the thermally stable and labile polymer in order to investigate influence of the PVP concentration on the gas permeance. The permeation results showed decreased permeances for the carbon membranes prepared by the PVP concentration of 0.6 wt% or lower. At higher PVP concentration, the permeances especially for the gas species with larger molecular size increased due to increased membrane structure and the enhanced diffusional pathways for the gas transport through carbon membranes. It is considered that the addition of the thermally labile polymer can control the pore structure for the preparation of the carbon membrane derived from the PPO/PVP with different PVP concentrations.

Acknowledgements

Funding of this work and a research grant by the Japanese Society for the Promotion of Science (JSPS) is gratefully acknowledged. Also, this work was partly supported by the 2004 National Research Lab (NRL) Project [M 10400000061-04J0000-06110] administered by the Korean Ministry of Science and Technology (MOST).

Reference

1. A.F. Ismail and L.I.B. David, "A review on the latest development of carbon membranes for gas separation." *J. Membr. Sci.*, 193, 1 (2001).
2. B. Kruczek and T. Matsuura, "Development and characterization of homogeneous membranes from high molecular weight sulfonated polyphenylene oxide." *J. Membr. Sci.*, 146, 263 (1998).
3. S.M. Saufi and A.F. Ismail, "Fabrication of carbon membranes for gas separation- a review." *Carbon*, 42, 241 (2004).
4. H. Hatori, T. Kobayashi, Y. Hanzawa, Y. Imura, T. Kimura and M. Shiraishi, "Mesoporous carbon membranes from polyimide blended with poly(ethylene oxide)." *J. Appl. Polym. Sci.*, 79, 836 (2001).
5. Y.K. Kim, H.B. Park and Y.M. Lee, "Carbon molecular sieve membranes derived from their thermally labile polymer containing blend polymers and their gas separation properties." *J. Membr. Sci.*, 243, 9 (2004).