Influence of thermally labile polymer on gas separation properties of carbon membranes derived from poly(2,6-dimethyl-1,4-phenylene oxide)

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Abstract

Interests on gas separation using inorganic membranes have increased due to good thermal and chemical stabilities. In this study, the carbon membranes derived the thermally stable and labile polymer blends were prepared using polymer blends of poly(2,6-dimethyl-1,4-phenylene oxide)(PPO)/ Polypyrrolidone (PVP). The characterization of the pore structure confirmed that the addition of the thermally labile polymer decreased the pore volume and surface area. The permeation results for the PPO/PVP derived carbon membranes showed a strong dependency upon PVP molecular weight and concentration. The PPO/PVP derived carbon membranes with the low molecular weights showed decreased gas permeances and the increased permselectivity due to decrease in the pore structure. Meanwhile, increase in gas permeance was observed for the carbon membranes prepared high molecular weights due to the enhanced diffusional pathways for the gas transport through carbon membranes. It is considered through the permeation results for the carbon membrane derived from the PPO/PVP that the introduction of the thermally labile polymer lead to control the pore structure as a function of molecular weight.

Keywords: Carbon membrane, Poly(2,6-dimethyl-1,4-phenylene oxide), Polypyrrolidone, Gas permeation, Permeability

1 Introduction

Interests on gas separation using inorganic membranes have increased due to good thermal and chemical stabilities [1,2]. Of inorganic membranes, carbon 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 [3]. 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 pyroslysis at a desired temperature [4]. Recently, the gas permeation properties of carbon membranes derived from polyimide, polyacrylonitirle, poly(furfuryl alcohol) and phenolic resins. Of the above polymers, polyimde has been extensively used as a polymeric precursor through the synthesis of homo- or co-polymers for the carbon membrane preparation [5]. Among polymeric precursors, poly(2,6-dimethyl-1,4-pyphenylene oxide) (PPO) having a high glass transition temperature is considered as one of the alternative promising polymeric materials for carbon membrane preparation [6].

It is known that carbon membrane pore structures can be modified by the post-treatment methods such as chemical vapor deposition and post-oxidation [5]. One of the other 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 [7]. To date, the thermally labile polymers, such as poly(vinyl butyral) (PVB) [8] and poly(ethylene glycol) (PEG) [9] and polypvinylpyrrolidone (PVP) [10,11] were considered as pore-forming agents. It was observed that carbon membranes derived from the polymer blend of polyimide and PVP with different molecular weights and blend ratio showed a high permeability and selectivity even though the carbonized membranes still had a microporous structure in the nitrogen adsorption results [11].

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, pretreatment, and pyrolysis of the polymeric precursor. The influences of the PVP molecular weight in the polymer blend PPO/PVP on the permeation performances were investigated and the results were compared with those of the carbon membrane derived from PPO.

2 Experimental

The polymeric membranes were prepared on the surface of a tubular macroporous ceramic support (NOK, Japan) having the average pore size of 100 nm and the porosity of 41.0 %. The PPO polymer (Aldrich Chemical Co., USA) was used as received as a thermally stable polymer. As a thermally labile polymer, different molecular weights of PVP were used such as 10 K, 29 K, 40 K, 55 K (Aldrich Chemical Co., USA) and 90 K (Wako Chemical Co., Japan). The polymer blend was prepared with 2.4 wt% of PPO and 0.6 wt% of PVP in chloroform. The carbon membranes were prepared by the preoxidation of the coated PPO polymer on the support in the stagnant air condition, followed by the pyrolysis [12]. The carbonization was performed by heating up to the pyrolysis temperature (700 ^{o}C) in the Ar atmosphere.

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 measured under the Ar atmosphere using a thermogravimetric analyzer (TG-DTA2000SA, Bruker AXS). The pore properties of pyrolyzed carbon materials were characterized by the nitrogen adsorption at -196 ^{o}C using an automatic adsorption apparatus (BELSORP-18, BEL Japan, Inc.) after the pyrolyzed carbon materials were pretreated at 300 ^{o}C during 5 hours in the vacuum condition. Also, the adsorption amount of CO_2 was measured for the pyrolyzed carbon materials at 25 ^{o}C.

Gas permeance of selected gas species, He (2.6 Å), CO_2 (3.3 Å), N_2 (3.64 Å) and CH_4 (3.8 Å) and C_2H_6 (4.0 Å), was measured using a permeation apparatus having a film flow meter (STEC, Japan) at the permeation temperature of 150 ^{o}C. The effect of the pyrolysis temperature on the permeation properties was considered for the carbon membrane derived from the polymer blend. Also, the influence of the PVP molecular weight on the gas permeation performance was investigated and the results were compared with those of the PPO derived carbon membrane. The permselectivity in the gas permeation experiments was estimated as the ratio of the permeance of each gas species.

3 Results and discussion

The thermal decomposition behaviors of PPO, PVP and the polymer blend of PPO/PVP were observed during the heating up to 1000 ^{o}C. PPO was stable up to approximately 420 ^{o}C, while PVP started to decompose at the temperature of 380 ^{o}C [13].

The total weight loss of the thermally labile polymer was measured to 80 % when the temperature reached to 450 ^oC. Meanwhile, the thermal gravimetric plot of PPO shows that the polymer structure started to degrade between 420 and 480 ^oC and developed the carbonized structure at around 600 ^oC. For the polymer blend of PPO/PVP, the decomposition occurred at the temperature of 420 ^oC, similar with PPO. At higher temperatures, the weight loss of PPO/PVP was more than PPO. The weight loss of PVP having a low thermal stability was 87 %, while that of PPO and PPO/PVP was 75 % and 77 %, respectively. The nitrogen adsorption result represents the Type I adsorption isotherm, indicating that the PPO carbonized material pyrolyzed at 700 ^oC has a microporous structure. In addition, the representative peak diameter of the carbon material was estimated to 0.43 nm by the HK (Horvath and Kawazoe) method in the pore size distribution. In the analysis result of the BET adsorption isotherm based on the nitrogen adsorption, the pore volume and the surface area for the carbon material were estimated to be 26.82 cm^3/g and 116.75 m^2/g, respectively. The CO_2 adsorption was measured at 25 ^oC for the carbon materials of PPO and PPO/PVP and the characteristic values were estimated and the results were shown in Table 1. Considering the BET pore volume and surface area for the carbon materials prepared by the PPO/PVP blend, the characteristic values decreased compared with the carbon material of PPO.

Table 1 Characteristic values for carbon materials based on the CO_2 adsorption measurements

Carbon material	PPO	PPO/PVP blend
BET pore volume (cm^3/g)	78.21	66.81
BET surface area (m^2/g)	409.84	350.13

. The influence of the PVP molecular weight on the permeation performance was investigated in the permeation results for the carbon membranes with PVP different molecular weights at the polymer blend at the PVP concentration of 0.6 wt% and the results were compared with those of the PPO derived carbon membrane. Fig. 1 shows the permeance of gas species for the carbon membranes derived from PPO and PPO/PVP blends at the permeation temperature of 150 ^oC. 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 the high PVP molecular weights (55K and 90K). Also, the carbon membranes prepared with low PVP molecular weights showed decreased permeances compared with the PPO derived carbon membrane.

Based on the permeation results, the influence of the molecular weights on the permselectivity was investigated and the results were shown in Fig. 2 In the case of He/CO_2, the estimated values were increased with increasing molecular weight and then decreased at higher molecular weights than 40 K. In the result of CO_2/CH_4 with increasing molecular weight, it was observed that the estimated value was decreased by the PVP addition. The addition of low PVP molecular weight decreased permeance due to the similar thermal decomposition behavior of PPO and PVP. Meanwhile, the permeation results for the carbon membranes derived from high PVP molecular weights increased permeance due to a diffusional pathway [10,11].

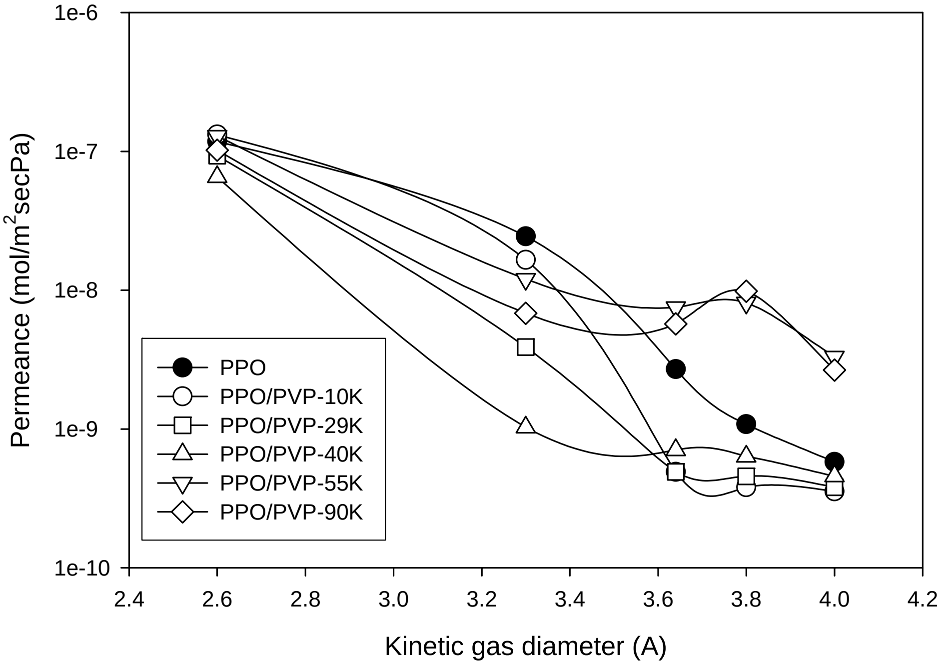

Fig. 1. Gas permeance for the carbon membranes prepared with different PPO molecular weights.

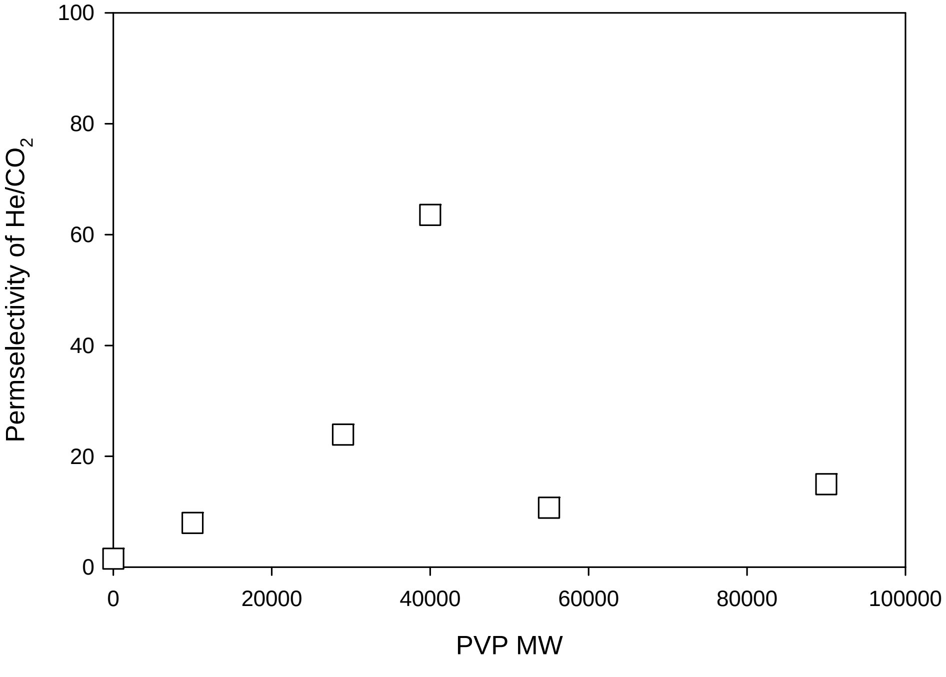

Fig. 2. Influence of PVP molecular weight on the permselectivity (He/CO_2) for the carbon membranes.

4 Conclusions

In this study, the carbon membrane derived PPO/PVP precursor was prepared using a polymer blend of the thermally stable and labile polymer and the influence of the PVP molecular weight on the permeation performance was investigated. The characterization of the pore structure confirmed that the addition of the thermally labile polymer decreased the pore volume and surface area. The permeation results for the PPO/PVP derived carbon membranes prepared with the low molecular weights (up to 40 K) decreased gas permeances and the increased permselectivity due to decrease in the pore structure. The pemselectivity of gas pairs of small molecular size (He/CO_2) was increased up to 64 at the PVP molecular of 40 K. In the permeation results for the carbon membranes prepared with high molecular weights, increase in gas permeance was observed due to 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 blend.

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