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Preparation of Carbon Membranes Derived from Polymer Blends in the Presence of a Thermally Labile Polymer

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Abstract: Carbon membranes for gas separation were prepared from the polymer blend consisting of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polyvinylpyrrolidone (PVP) as the thermally stable and labile polymer, respectively. The PPO/PVP derived carbon membranes with lower PVP concentrations than 0.6 wt% showed decreased gas permeances and increased permselectivity due to decrease in the pore properties (pore volume and surface area). Meanwhile, gas permeance increased for the carbon membranes prepared with higher PVP concentrations than 0.6 wt% due to the enhanced diffusional pathways for the gas transport through carbon membranes especially in the domain of the thermally labile polymer. It is considered that the introduction of the thermally labile polymer leads to control the pore structure through the permeation results for the carbon membrane derived from the polymer blend.

Keywords: Carbon membrane, gas permeation, poly(2,6-dimethyl-1,4-phenylene oxide), polyvinylpyrrolidone

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INTRODUCTION

The interests on gas separation using inorganic membranes including zeolite, ceramic and carbon membranes have increased due to good thermal and chemical stabilities compared with glassy polymeric membranes (1–3). Attractive opportunities for gas separation are found in the various application areas, such as natural gas processing, acid gas treatment, landfill gas recovery, olefin/paraffin separation, air separation, and hydrogen recovery (4, 5). Of inorganic membranes, carbon membranes are considered to be one of the most promising materials for membrane-based gas separation because it has excellent permeation and separation properties and thermal and chemical stability even under harsh conditions, such as high pressure and high temperature (6).

The preparation of carbon membranes involves the following steps: polymer precursor selection, polymeric membrane preparation, preoxidation, pyrolysis/carbonization, post-treatment, and module construction (7). It is generally known that the gas permeation properties of carbon membranes are mainly affected by the polymeric precursor, pyrolysis conditions, and post-treatment conditions (8). The selection of a polymeric precursor is the most important step since it can yield a series of membranes having micropores of desired molecular dimensions through the pyroslysis at a desired temperature (9). Recently, the gas permeation properties of carbon membranes derived from polyimide, polyacrylonitrile, poly(furfuryl alcohol), and phenolic resins. Of the above polymers, polyimide has been extensively used as a polymeric precursor through the synthesis of homo- or copolymers for the carbon membrane preparation by now (8).

It is known that the pore properties of carbon membranes can be modified by the post-treatment methods such as chemical vapor deposition and post-oxidation. One of the modification methods is to carbonize a 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 (10, 11). To date, the thermally labile polymers, such as poly(vinyl butyral) (PVB) (12) and poly(ethylene glycol) (PEG) (13, 14) and polyvinylpyrrolidone (PVP) (15, 16) 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 (15, 16).

Among thermally stable polymers, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) having a high glass transition temperature is considered as one of the alternative promising polymeric materials for carbon membrane preparation (17, 18). 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 (19, 20). The correlation of the permeability and the selectivity for PPO polymer membranes showed the closeness to the Robeson line, the upper bound line for polymer membranes (21). Still, the permeation performance of the PPO polymer membranes was affected by the chemical and thermal instability, showing trade-off of permeability and selectivity. Therefore, it is necessary to prepare carbon membranes which are chemically and thermally stable compared with PPO polymer membranes in order to increase the applicable potentials. Until now, the preparation of carbon membrane derived PPO polymer and the permeation results have been rarely reported (22, 23).

In this study, the carbon membranes derived from a polymer blend of the thermally stable polymer (PPO) and the thermally labile polymer (PVP) were prepared by the consecutive steps, preparation of polymeric membrane on the support surface, preoxidation, and pyrolysis of the polymeric precursor. The influences of the preparation conditions on the permeation performances were investigated for the carbon membranes.

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EXPERIMENTAL PROCEDURE

The PPO polymer (Aldrich Chemical Co., USA) was used as received as a thermally stable polymer for the carbon membrane preparation. As a thermally labile polymer, the molecular weight of 40 K PVP (Aldrich Chemical Co., USA). The polymer blend ratio of PPO and PVP was varied, the total concentration being set to 3.0 wt% in chloroform. The solvent was removed by drying in the vacuum condition for 24 hours before preoxidation. Table 1 shows the various polymer blends of PPO and PVP with a different ratio. The carbon membranes were prepared by the preoxidation of the dip-coated polymer on the tubular type of the α-alumina ceramic support (NOK, Japan) having the mean pore size of 100 nm in the stagnant air condition, followed by the pyrolysis (8, 23). The carbonization was

Table 1. Preparation of the various carbon materials and membranes derived from PPO/PVP blends (PVP molecular weight: 40 K)

	PPO concentration (wt%)	PVP concentration (wt%)
PPO	3.0	0
PPO/PVP5	2.85	0.15
PPO/PVP10	2.7	0.3
PPO/PVP20	2.4	0.6
PPO/PVP30	2.1	0.9
PPO/PVP50	1.5	1.5

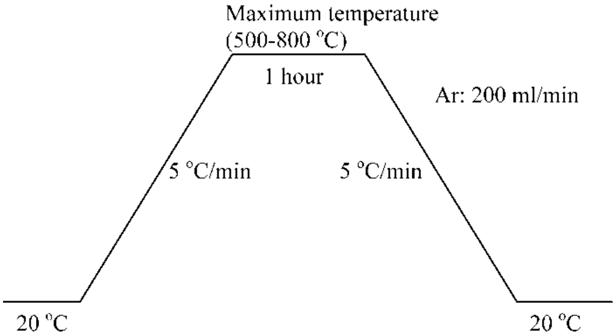

Figure 1. Temperature setup for the pyrolysis of the carbon membranes.

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performed by heating up to the pyrolysis temperature and cooling (rate of heating and cooling: 5°C/min) in the Ar atmosphere (flow rate: 200 ml/min). For the pyrolysis of the polymer blends, the maximum pyrolysis temperature was varied from 500 to 800°C at the duration time of 1 hour. Figure 1 shows the temperature setup for the pyrolysis of the carbon membranes.

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 polymer was measured under the Ar atmosphere (heating rate: 5°C/min and flow rate: 200 ml/min) using a thermogravimetric analyzer (TG-DTA2000SA, Bruker AXS). The pore properties of pyrolyzed carbon materials were characterized by the nitrogen adsorption at 77K using an automatic adsorption apparatus (BELSORP-18, BEL Japan, Inc.). The adsorption amount of CO_2 was measured for the pyrolyzed carbon materials at 25°C.

The permeance of the carbon membranes toward selected gas species, He (0.26 nm), CO_2 (0.33 nm), N_2 (0.36 nm), and CH_4 (0.38 nm), and C_2H_6 (0.40 nm), was measured using a permeation apparatus having a film flow meter (STEC, Japan) at the permeation temperature of 150°C. The kinetic gas diameter in the parenthesis was calculated from the minimum equilibrium cross-sectional diameter described by the Lennard-Jones potential (24). The permeation experiments were carried out in the feed pressure of about 3 atm and the permeate pressure of 1 atm, pressure difference being about 2 atm. The effect of the pyrolysis temperature on the permeation properties was considered for the carbon membrane derived from the polymer blends. Also, the influences of the pyrolysis temperature and the blend ratio of PVP on the gas permeation performances were investigated and the results were compared with those of the PPO derived carbon membrane. The permeances were measured at least three times for the duplicate carbon membranes. The permselectivity in the gas permeation experiments was estimated as the ratio of the permeance of each gas species.

RESULTS AND DISCUSSION

Characterization of the Carbon Materials

The thermal decomposition behaviors of PPO, PVP, and the polymer blend of PPO/PVP were observed during the heating up to 1000°C and Fig. 2 shows the weight loss of polymeric precursors with increasing temperature in the Ar atmosphere. As shown in the figure, PPO was stable up to approximately 420°C, while PVP started to decompose at the temperature of 380°C (25). The total weight loss of the thermally labile polymer was measured to 80% when the temperature reached to 450°C. Meanwhile, the thermal gravimetric plot of PPO shows that the PPO polymer structure started to degrade between 420 and 480°C and developed the carbonized structure at around 600°C. The polymer blend containing 0.6 wt% PVP (PPO/PVP20) started to decompose at the temperature of 420°C, similar with the result of PPO. At higher temperatures than 600°C, the weight loss of PVP having a low thermal stability was 87%, while that of PPO and PPO/PVP was 75% and 77%, respectively.

Based on the nitrogen adsorption results, the representative peak diameter of the carbon material pyrolyzed at 700°C was estimated to 0.43 nm by the HK (Horvath and Kawazoe) method as shown in Fig. 3. In the analysis result of the BET adsorption isotherm, the pore volume and the surface area for the PPO derived carbon material were estimated to be 26.8 cm^3/g and 116.8 m^2/g,

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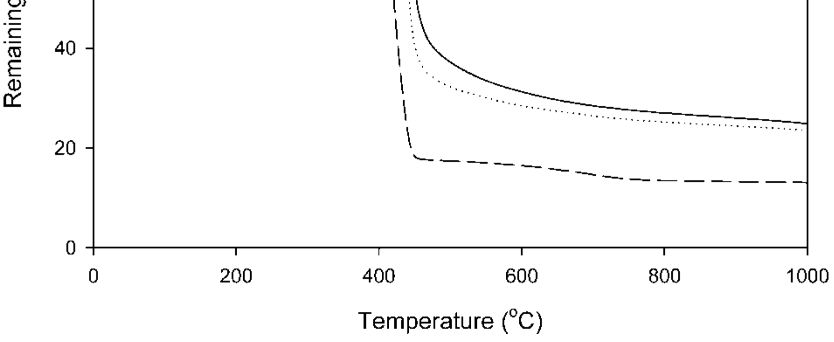

Figure 2. Thermal decomposition of the polymeric precursors.

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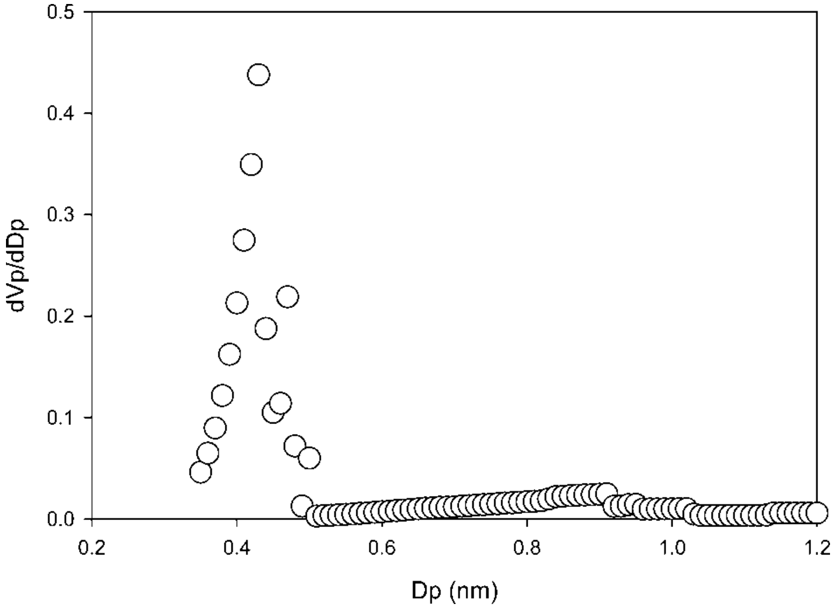

Figure 3. Pore size distribution of the PPO derived carbon material pyrolyzed at 700°C by the nitrogen adsorption.

respectively. The CO_2 adsorption was measured at 25°C for the carbon materials of PPO and PPO/PVP since the nitrogen adsorption amounts were small for the PPO/PVP blend. Based on the CO_2 adsorption measurements, the characteristic values were estimated and the results were shown in Table 2. 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 as the PVP concentration increased up to 0.6 wt%. At higher PVP concentration, it is

Table 2. Characteristic values for carbon materials based on the CO_2 adsorption measurements

Carbon material	PPO	PPO/PVP blend		
		PPO/PVP10	PPO/PVP20	PPO/PVP50
BET pore volume (cm^3/g)	78.2	66.8	53.1	85.8
BET surface area (m^2/g)	409.8	350.1	277.9	420.6

suggested that the pore structure enlarged due to the domain of the thermally labile polymer (10). It is considered that the addition of the thermal labile polymer changed pore volume and surface area of carbon pore structures in the results for the CO_2 adsorption measurements.

Influence of Pyrolysis Temperature on the Permeation Properties

In a SEM microphotograph, it was observed that the carbon layer of the carbon membranes derived from PPO and PPO/PVP blends on the macroporous support surface has the thickness of 3.0 ± 0.2 μm. The PPO/PVP carbon membranes were prepared at different pyrolysis temperatures in order to investigate the influence of the pyrolysis temperature on the permeation properties. Figure 4 shows the permeance as a function of kinetic gas diameter. In the figure, PPO/PVP20-P500 denotes the carbon membrane pyrolyzed at 500°C using the polymer blend of PPO/PVP20 containing 0.6 wt% of PVP. As shown in the figure, the carbon membranes prepared at 500 and 600°C showed high permeances for all examined gas species. However, the permeation results showed decreased values for the carbon membranes prepared at higher pyrolysis temperature (700 and 800°C). The permeation results imply that the carbonized structure developed in the PPO/PVP blend carbon membranes at high pyrolysis temperature.

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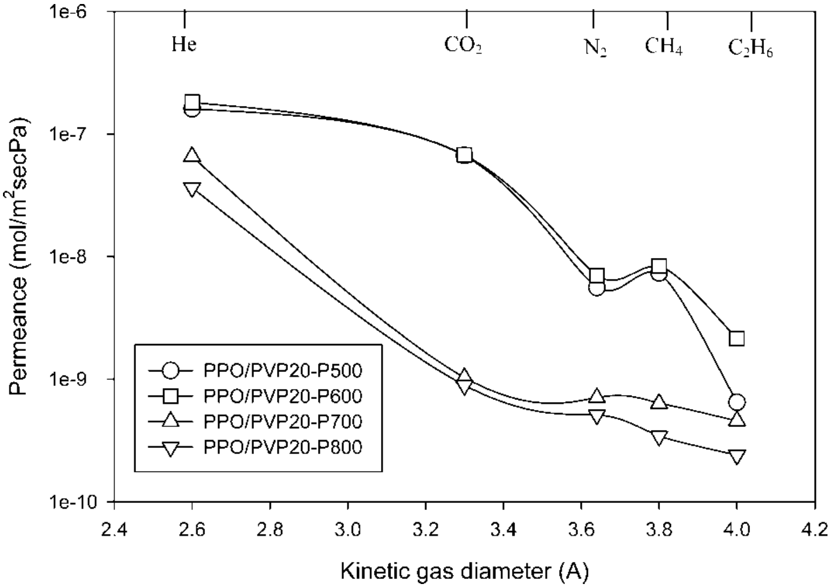

Figure 4. Permeance of gas species for the carbon membranes derived from the polymer blend of PPO/PVP20 blend with different pyrolysis temperature (Permeation temperature: 150°C).

Table 3. Permselectivity for the carbon membrane derived from a polymer blend with different pyrolysis temperature (Polymer blend: PPO/PVP 20, permeation temperature: 150°C)

Pyrolysis temperature (°C)	He/CH_4	He/N_2	He/CO_2
500	22	29	2
600	22	26	3
700	103	93	64
800	106	71	41

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Table 3 shows different behaviors with increasing pyrolysis temperature for the PPO/PVP blend carbon membranes. At the low pyrolysis temperature (600°C), the permselectivity of He/CH_4 and He/N_2 was 22 and 26, as shown in the table. Meanwhile, the permeation results for the carbon membrane prepared at 700°C showed increased value as 103 and 93 for He/CH_4 due to decrease in the pore characteristic values (23). It is interesting that the permselectivity of He/CO_2 was increased from 3 (600°C) to 64 (700°C) due to decrease in CO_2 permeance. The permeation result can be explained by the fact that the characteristic pore properties were decreased at high pyrolysis temperature (23). In the permeation results for the carbon membranes prepared with different pyrolysis temperatures, it is suggested that the pyrolysis at high temperatures decreased pore structures. Based on the permeation results, the pyrolysis temperature was determined as 700°C for preparation of the carbon membranes derived from PPO/PVP.

Influence of PVP Concentration on the Permeation Properties

Gas permeation properties of carbon membranes prepared by the pyrolysis at 700°C were evaluated using single gas permeation experiments at the permeation temperature of 150°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°C (See Fig. 5). The permeation results of all the carbon membranes showed that the gas transport was controlled by the molecular sieving mechanism for the carbon membranes prepared by lower PVP concentrations than 0.6 wt%. It is assumed that the carbon membrane prepared with high PVP concentrations (PPO/PVP30 and PPO/PVP50) provided an enhanced diffusional pathway for the gas species in the domain of the thermally liable polymer (15, 16).

Considering increase in the gas permeance for the carbon membranes with different PVP concentration, the permeance of He showed relatively similar values for examined PVP concentrations. Meanwhile, the permeance

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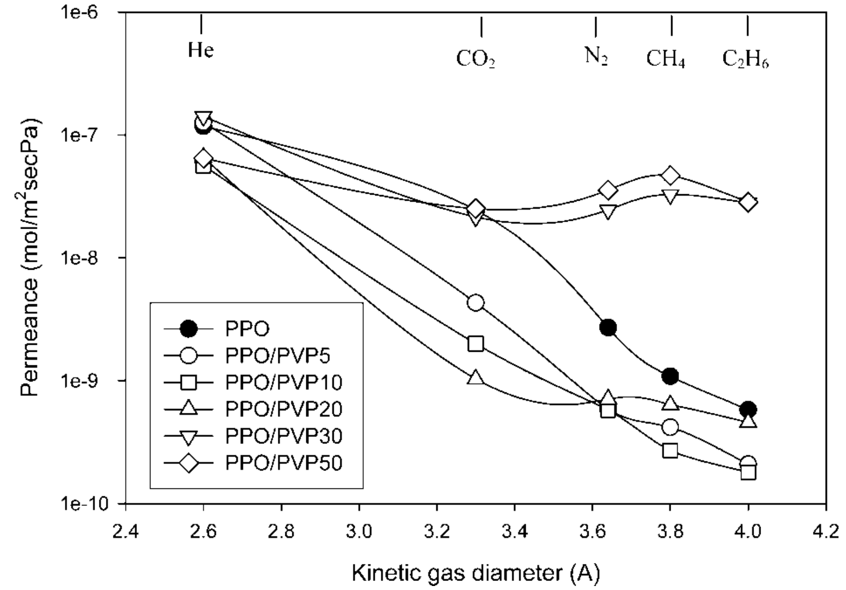

Figure 5. Permeance of gas species for the carbon membranes derived from PPO and PPO/PVP blends with different blend ratio (Permeation temperature: 150°C).

of N_2, CH_4, and C_2H_6 decreased for the carbon membranes prepared by the PVP concentration of 0.6 wt%. The permeation results imply that the addition of PVP with low concentrations decreased pore structures, which was discussed before. However, the carbon membranes of PPO/PVP30 and PPO/PVP50 showed increased permeance of N_2, CH_4, and C_2H_6. The N_2 permeance showed increased values about ten times for both membranes compared with the permeation result of the PPO derived carbon membrane. Considering the CO_2 adsorption results shown in Table 2, PPO/PVP30 showed decreasing values of pore volume and surface area. In the case of the addition of PVP with high concentrations (e.g. 0.9 and 1.5 wt%), however, the permeances notably increased up to about 10–50 times compared with the PPO derived carbon membrane. The carbon membranes derived from PPO/PVP with low concentrations showed decreased permeance and increased permselectivity.

Figure 6 shows the influence of the PVP concentration on the permselectivity for the carbon membranes derived from PPO/PVP blend. In the permselectivity of He/CO_2 in Fig. 6(a), the estimated value increased with increasing PVP concentration up to 0.6 wt%. The permselectivity value of He/CO_2 for the carbon membrane of PPO/PVP was about 64 due to decrease in the pore structure. Considering the permselectivity of CO_2 with gas species having larger kinetic diameter, CH_4, the estimation results showed significantly low values compared with the carbon membrane of

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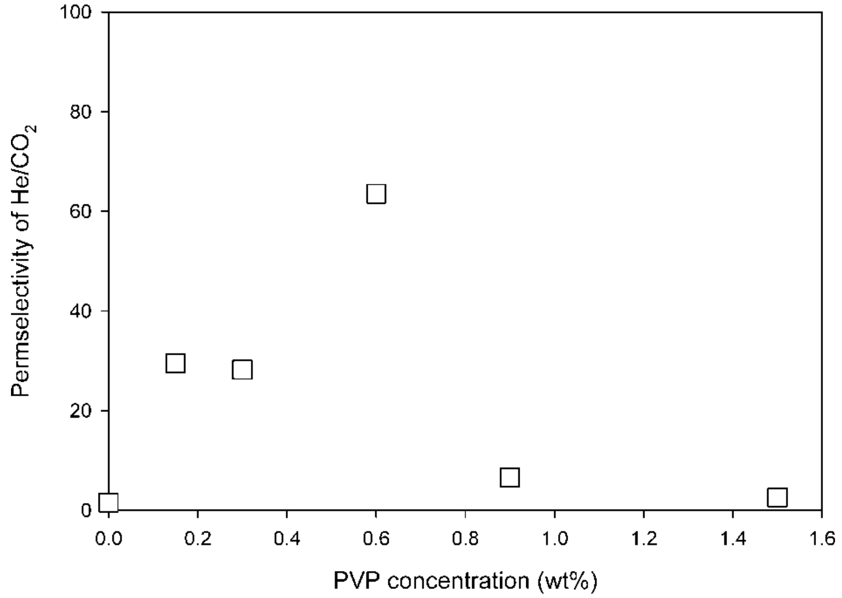
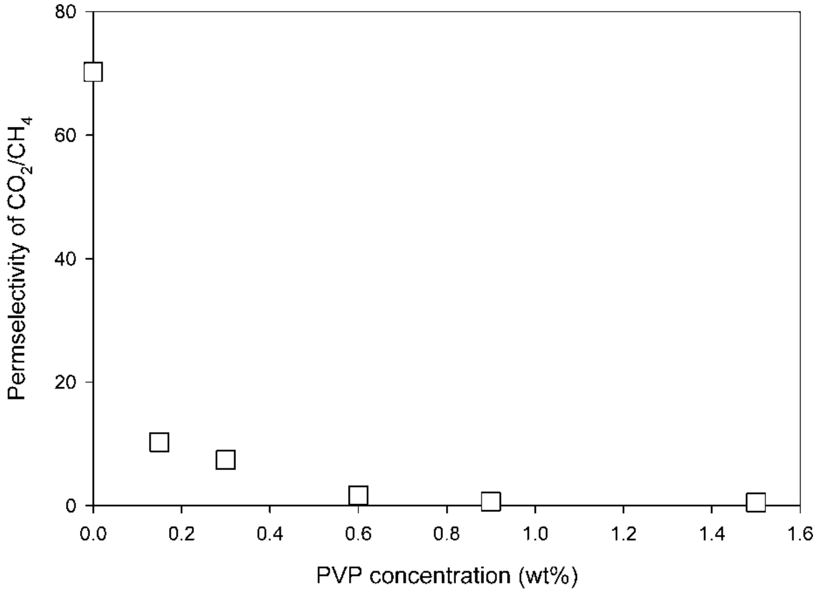


(a) Permselectivity of He



(b) Permselectivity of CO$_2$

Figure 6. Influence of PVP concentration on the permselectivity for the carbon membranes (Permeation temperature: 150°C).

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PPO (0 wt% of PVP concentration). The permselectivity of CO_2/CH_4 in Fig. 6(b) was 70 for the PPO derived carbon membrane, and then decreased with increasing PVP concentration. The permeation results shown the figure imply that the PVP addition decreased the pore structure of the membrane structure, giving a significant effect on CO_2 permeance.

Based on the permeation results, the relationship between the permeability and the permselectivity was considered for the carbon membranes derived from the PPO/PVP blends and the results were compared with that of the PPO derived carbon membrane pyrolyzed at 700°C. Figure 7 shows the correlations of the permeability and the permselectivity for the system of He/CH_4 with the Robeson's line (21). The correlation of the He permeability and the permselectivity of He/CH_4 show higher permeation performance compared with the Robeson's line for the carbon membranes prepared by lower concentrations than 0.6 wt%. Some of the permeation data showed increased permselectivity (between 103 and 347), about 10–20 times higher than the result of the PPO derived carbon membrane ($He/CH_4 = 16$).

The permeability of He existed within 300 and 1000 barrers (1 barrer $= 7.502 \times 10^{-15}$ m^3(STP) m/(m^2 sec kPa)) in the carbon membranes derived from the PPO/PVP blends having higher PVP concentrations than 0.6 wt%. Of the carbon membranes, the results for PPO/PVP5 showed increased values of the permeability and the permselectivity than the PPO carbon membrane. It is considered that the addition of the thermally labile polymer can control the pore structure of carbon membranes with different pyrolysis temperature and polymeric concentration.

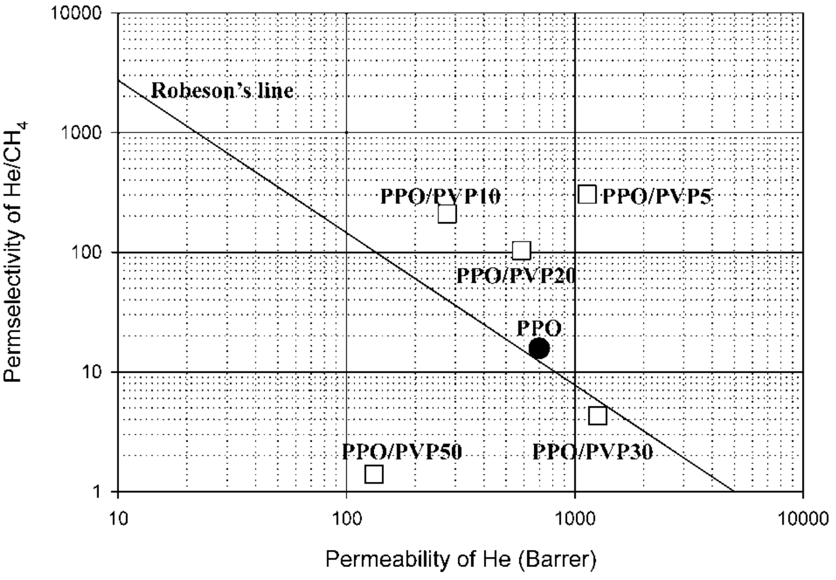

Figure 7. Correlation between permeability and permselectivity of He and CH_4.

CONCLUSIONS

The carbon membranes derived PPO/PVP precursors were prepared using a polymer blend of the thermally stable and labile polymer. The characterization of the pore structure confirmed that the addition of the thermally labile polymer decreased the pore volume and surface area at lower PVP concentrations than 0.6 wt%. The permeation results for the PPO/PVP derived carbon membranes prepared by the low concentrations decreased gas permeances and the increased permselectivity due to decrease in the pore structure. In the permeation results for the carbon membranes prepared with higher concentrations than 0.6 wt%, gas permeances increased due to the enhanced diffusional pathways for the gas transport through carbon membranes in the domain of the thermally unstable polymer. 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 preparation conditions, such as pyrolysis temperatures and PVP concentrations.

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