

열분해성 고분자 도입에 따른 탄소분자체막의 기체 투과 특성

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

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요 약: Polyvinylpyrrolidone을 포함하는 폴리이미드 전구체의 열분해 공정을 통해 탄소분자체막을 제조하였으며 열분해성 고분자를 포함하는 전구체를 통해 제조된 막의 구조 및 기체 투과 특성에 대해 연구 하였다. 열분해성 고분자를 포함하는 전구체의 열적 특성을 조사한 결과 열적으로 안정한 폴리이미드의 경우 550°C에서 분해되는 것을 확인할 수 있었으며 열분해성 고분자의 경우 400°C에서 분해가 시작되는 것을 TGA를 통해 확인하였다. 제조된 탄소분자체막의 기체 투과 특성을 조사한 결과 최종 열분해 온도가 증가 됨에 따라 기체 투과도는 감소하였으며 열분해성 고분자를 포함한 전구체로부터 제조된 탄소분자체막의 경우 기체 투과가 향상 됨을 알 수 있었다. 열분해성 고분자를 함유하는 전구체로부터 550°C에서 열분해를 통해 제조된 탄소분자체막의 경우 O₂ 투과도 808 Barrer [$10^{-10} \text{ cm}^3 \text{ (STP)cm/cm}^2\text{scmHg}$]과 O₂/N₂ 선택도 7을 나타내었다.

Abstract: Carbon molecular sieve (CMS) membranes were prepared by the pyrolysis of polyvinylpyrrolidone containing polyimide precursors. We have prepared the polymer precursors, pyrolyzed polymer and investigated the effect of pyrolyzing polymer on the characteristics of carbon structures and gas separation properties of the CMS membranes. Thermogravimetric analysis (TGA) showed the two-step decomposition of polymer precursor. First decomposition of the pyrolyzing polymer began around 400°C while carbonizing polymer showed the decomposition around 550°C. The gas permeabilities through the CMS membranes were enhanced by the introduction of the pyrolyzing polymer and decreased with increased final pyrolysis temperature. The CMS membrane pyrolyzed at 550°C derived from precursor containing 5wt% PVP as a pyrolyzing polymer showed gas permeability for O₂ of 808 Barrers [$10^{-10} \text{ cm}^3 \text{ (STP)cm/cm}^2\text{scmHg}$] and O₂/N₂ selectivity of 7.

Keywords: carbon molecular sieve membrane, pyrolyzing polymer, polyimide, polyvinylpyrrolidone, gas separation

1. Introduction

Carbon molecular sieve (CMS) membranes have numerous advantages compared with polymeric membranes. The main advantage is that the CMS membrane is suitable for separating gas mixtures with similar

molecular sizes such as O₂/N₂, CO₂/CH₄, and CO₂/N₂ [1]. Since Koresh and Soffer reported the preparation of carbon membrane in 1983 [2], various types of carbon membranes have been prepared from polyfurfuryl alcohol, polyvinylidene chloride-acrylate terpolymer, phenol resin, acrylonitrile-methyl methacrylate copolymer, polyimide, polypyrrolone and polyaromatic resin [3-10]. In particular, polyimides were found to give a graphite

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Table 1. CMS Membranes Derived from Polyimide Polymer Precursors

Investigator	Membrane (precursor)	Ref.
Hatori et al.	Kapton-type polyimide ^a	[8]
Koros et al.	6F-containing polyimide copolymer ^b	[9]
Morroka et al.	BPDA-ODA	[12]
Suda et al.	Kapton-type polyimide ^a	[13]
Hayashi et al.	BPDA-ODA	[14]

^a: Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA).

^b: 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-bis-1,3-isobenzofurandione (6FDA), 3,4,3',4'-biphenyltetracarboxylic acid dianhydride (BPDA), and 2,4,6-trimethyl-1,3-phenylenediamine (tTDA)).

structure with rather high crystallinity through a simple heat treatment under atmospheric pressure [11]. Up to now, studies on CMS membranes have been focused on the types of precursors and pyrolysis conditions (pyrolysis temperature, pyrolysis protocol, heating rate, and pyrolysis atmosphere). The CMS membranes derived from polyimide precursors have been mostly considered in the numerous studies as listed in Table 1.

In this study, we prepared the CMS membranes by pyrolysis polymer precursors containing pyrolyzing polymer. In the case of CMS membranes prepared by pyrolysis of polymer precursor containing pyrolyzing polymer [15-18], the CMS membranes formed two different porous carbon structures. The decomposition of pyrolyzing polymer builds up the mesoporous (2-50 nm) carbon structures and the carbonizing polymer lead to the formation of microporous (<2 nm) carbon structures during the pyrolysis. Hatori and Ozaki prepared the carbon films by pyrolysis of poly(ethylene glycol) (PEG) [16] and poly(vinyl butyral) [17] as pyrolyzing polymers. From their results, they confirmed the presence of mesopores, and pyrolyzing polymer led to the development of mesoporous carbon structures. Furthermore, not only mesoporous but also macroporous (>50 nm) carbon structures can be obtained from a polymer blend as considered to correlate to the change of the phase-separation structure. In this paper, we prepared the CMS membranes derived from polyimide precursor containing polyvinylpyrrolidone (PVP) as a pyrolyzing polymer. Commonly, PVP was used as a pore-forming agent in the ultrafiltration (UF) membranes by phase inversion method. PVP controlled morphological structure and enhanced the performance of UF membranes

[19-21]. The goal of this study is to investigate the effect of pyrolyzing polymer on the characteristics of carbon structure and gas separation properties of CMS membranes.

2. Experimental

2.1. Preparation Precursors and CMS Membranes

Polyimide (PI) was synthesized with benzophenone tetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (ODA) and then polyvinylpyrrolidone (PVP, MW 55,000) used as pyrolyzing polymer. The BTDA and PVP were purchased from the Aldrich Chemical Co., (Milwaukee, WI, USA). ODA was purchased from the TCI Co., (Tokyo, Japan). Dimethyl sulfoxide (DMSO, Aldrich Chemical Co., Milwaukee, WI, USA, minimum assay 99%) was used after drying in 4 Å molecular sieves.

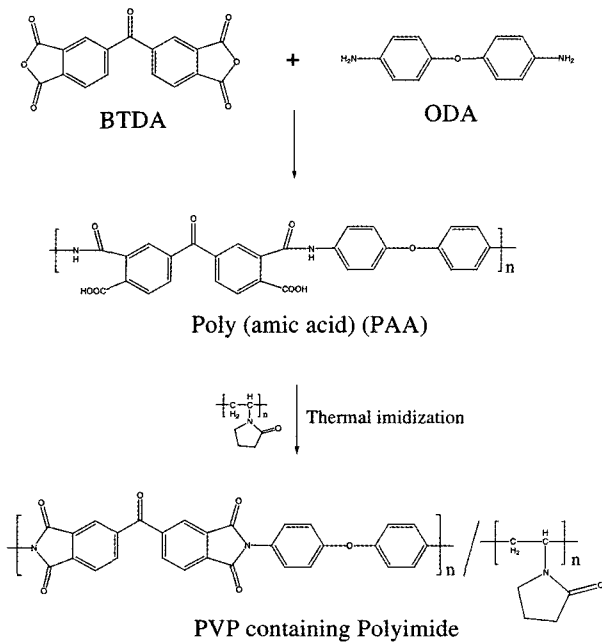
The PI/PVP precursor was prepared by a two-step procedure. The composition of precursors employed in this study is summarized in Table 2. First, ODA was dissolved in DMSO under a nitrogen atmosphere and a magnetic stirrer until gets a clear solution, and then the purified powder of BTDA was added to the ODA solved solution gradually. The reaction mixture was then stirred for 3 h at room temperature to yield a transparent yellow viscous poly(amic acid) (PAA) solution. Second, 5 wt% PVP (MW 55,000) was added to 20 wt% PAA solution, respectively. The chemical structures of compounds and reaction mechanism of PI/PVP precursors are illustrated in Fig. 1.

The polymer precursor was prepared by casting the PAA and PAA/PVP solution onto a glass plate, and

Table 2. The Composition of Precursors and CMS Membranes Prepared in This Study

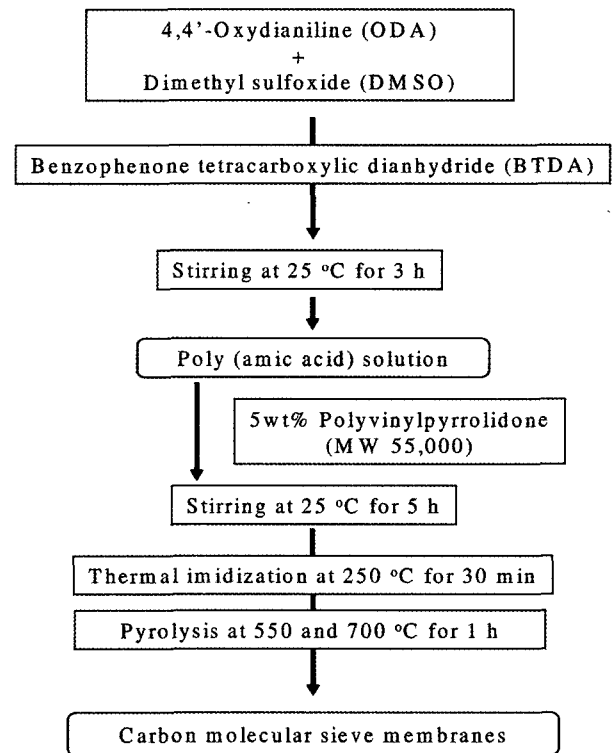
Precursors	CMS membranes	BTDA(mmol)	ODA(mmol)	M.W of PVP(5wt%)
PI	CMS 550 ^a	10	10	-
PI	CMS 700 ^b	10	10	-
PI-P55	CMS 550-P55 ^a	10	10	55,000
PI-P55	CMS 700-P55 ^b	10	10	55,000

^a Pyrolyzed at 550°C, ^b Pyrolyzed at 700°C

**Fig. 1.** Synthesis of polymer precursor.

the polymer solution was thermally imidized in a vacuum oven using the three-step imidization protocol: 50°C for 3 h, 100°C for 1 h, 200°C for 1 h and 250°C for 30 min, respectively. After imidization, the vacuum oven was allowed to gradually cool to the room temperature before the precursors were removed. The thickness of the precursor was approximately 30-40 μm . The preparation procedure of precursors and CMS membranes is shown in Fig. 2.

The CMS membranes were prepared by pyrolysis of their precursors at final pyrolysis temperatures of 550 and 700°C, respectively. The precursor was placed in the middle of a quartz tube and pyrolyzed under flowing argon gas (flow rate = 300 cm^3 (STP)/min) in a tube furnace supported on an alumina holder plate (see Fig. 3). The pyrolysis protocol used in this work was pre-determined using a thermogravimetric analyzer

**Fig. 2.** Precursors and CMS membranes preparation procedure.

(TGA). Fig. 4 shows the pyrolysis protocols used for an appropriate pyrolysis of the precursors.

2.2. Characterization of Precursors and CMS Membranes

Fourier transform infrared (FT-IR) spectra of the precursor and CMS membranes were measured using a Nicolet Magna IR 860 spectrometer (Thermo Nicolet, Madison, WI, USA) operating in the wavenumber range 4000-500 cm^{-1} to confirm the imidization reaction of precursors. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA2050 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA) to study the thermal properties of the PI and

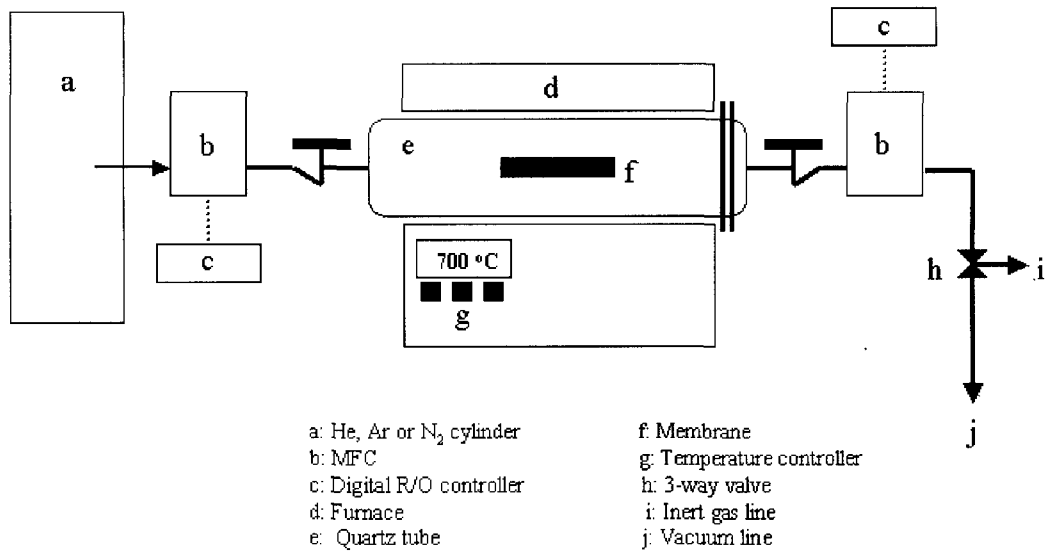


Fig. 3. Schematic diagram of the pyrolysis furnace used for inert purge protocols.

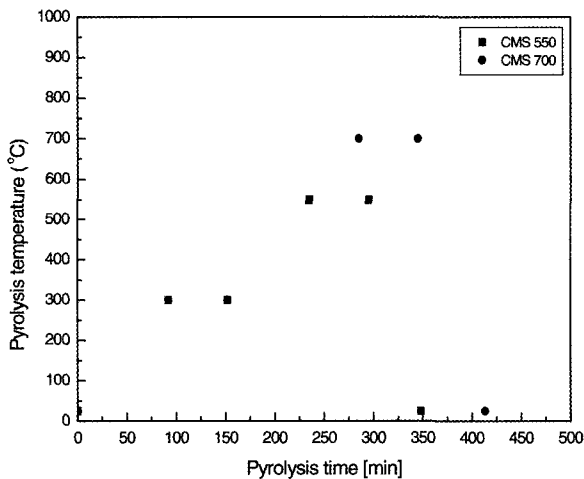


Fig. 4. Pyrolysis history of polymer precursor.

PI/PVP precursors. Wide-angle X-ray diffraction (WAXD) measurements were performed using a Rigaku Denki model RAD-C (Rigaku, Tokyo, Japan) with CuK α radiation of wavelength 1.54 Å to evaluate the d spacing of the CMS membranes after the pyrolysis.

2.3. Measurement of Gas separation Performance

The permeation properties of CMS membranes derived from PI and PI/PVP precursors were analyzed with different kinetic diameter of gas molecules: He (2.6 Å), CO₂ (3.3 Å), O₂ (3.46 Å), and N₂ (3.64 Å). The gas

permeabilities were measured using a single gas permeation technique by the time-lag method at a feed pressure of 760 Torr and a feed temperature of 25°C. The permeability, P , was obtained from the steady-state permeation rate, R , as

$$P = \frac{R/A}{\Delta p/l} \quad (1)$$

where A and l are the effective membrane area (cm²) and the membrane thickness (cm), respectively. ΔP (cmHg) is the pressure difference between the feed side (760 Torr) and permeate side ($<1 \times 10^{-5}$ Torr). The ideal separation factor (gas selectivity) for components 1 and 2 is defined as the ratio of the pure gas permeabilities of each component by the following equation:

$$\alpha_{1/2} = \frac{P_1}{P_2} \quad (2)$$

3. Results and Discussion

3.1. FT-IR Spectrum

The imidization of PI/PVP precursor was confirmed using FT-IR spectrum. As shown in Fig. 5, an absorption

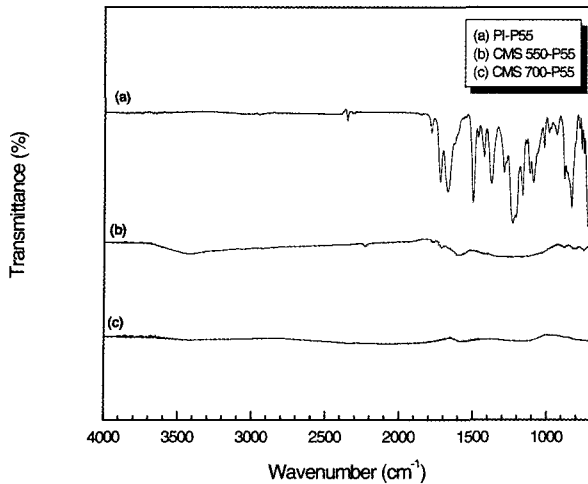


Fig. 5. FT-IR spectra of (a) PI/PVP precursors and CMS membranes pyrolyzed at (b) 550 and (c) 700°C.

bands at 1778 and 1724 cm^{-1} characteristic of the C=O stretching in imide groups were observed. An absorption band at 1371 cm^{-1} (CNC stretch) was observed, while an absorption band at 1569 cm^{-1} (NH group) was not observed in the spectrum. The observation of these bands clearly indicates the existence of imide groups, and confirms the successful preparation of PI/PVP precursors. When the FT-IR spectra of CMS membranes prepared at final pyrolysis temperatures of 550°C (CMS 550) and 700°C (CMS 700) are compared, the intensities of the absorption bands of the aliphatic or aromatic groups were reduced at elevated pyrolysis temperatures.

3.2. Thermal Stability

As shown in Fig. 6, the typical TGA thermograms of PI and PI/PVP precursors showed that PI precursor was stable up to approximately 550°C. The thermal stability of BTDA-ODA based polyimides was reported in the literatures [22,23]. The BTDA-ODA based polyimide confirmed the decomposition temperature in the range of 500-550°C. From the TGA thermograms, the weight of PI/PVP precursors reduced rapidly in the range of 400-450°C due to the exclusion of PVP. The thermal decomposition of the PI/PVP precursors proceeds through two stages. The first and second weight loss appeared due to the decomposition of PVP and PI,

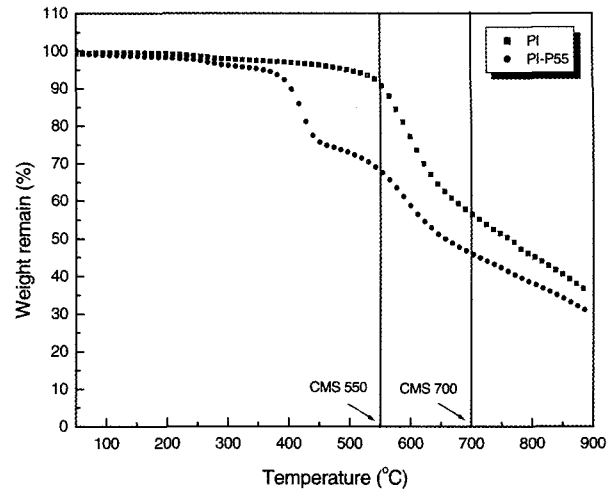


Fig. 6. Thermal gravimetric analysis of PI and PI/PVP precursors.

respectively. From the TGA thermograms, PI and PVP showed the different thermal decomposition phenomena. These results predict the different porous carbon structures of final CMS membranes after pyrolysis. These phenomena will be explained through the structural characteristics by WAXD data and gas permeation properties of CMS membranes.

3.3. Wide angle X-ray Diffractions

Wide angle X-ray diffraction (WAXD) can be used as a qualitative measurement of the interlayer spacing differences. The different regularity, ordered dimensions and morphologies of carbon structures should confirmed different WAXD patterns [24]. Regular ordered dimensions can be calculated from the Bragg equation

$$n\lambda = 2d \sin \theta \quad (3)$$

where d is the d spacing, λ is the diffraction angle, is the X-ray wavelength (1.54 Å), and n is an integral number (1, 2, 3, ...). Generally, X-ray diffraction is a useful tool for studying the organization of carbon on a molecular level. The changes of d spacing depend on the extent of heat treatment and can provide an indicator of the amount of available space to penetrate small molecules. Table 3 shows d spacing values of CMS membranes calculated from wide angle X-ray

Table 3. *d* Spacing Values of CMS Membranes Calculated from Wide Angle X-ray Diffraction Data

CMS membranes	<i>d</i> spacing [Å]
CMS 550	4.0
CMS 550-P55	4.3
CMS 700	3.6
CMS 700-P55	3.8

diffraction data. The *d* spacing of CMS membranes decreased with increasing the final pyrolysis temperature. Both CMS membranes pyrolyzed at 550 and 700°C containing PVP showed the increased of *d* spacing upon the addition of PVP. The structural differences of carbon matrix constituted by the final pyrolysis temperature and pyrolyzing polymer will affect the gas separation properties.

3.4. Gas Separation Performance of CMS Membranes

The gas separation performance through CMS membrane was investigated at 25°C for single gas permeants (He: 2.6 Å, CO₂: 3.3 Å, O₂: 3.46 Å, and N₂: 3.64 Å). In the present study, the permeation properties of CMS membranes were investigated concerning the final pyrolysis temperatures and the function of pyrolyzing polymer. As shown in Figs. 7 and 8, the permeabilities of CMS membranes decreased and the selectivities increased with increasing the final pyrolysis temperatures. Many researchers have explained

the relationship between the gas separation properties and final pyrolysis temperature [25-29]. The permeabilities of CMS membranes reduced by raising the final pyrolysis temperature due to the smaller effective pore sizes in the carbon matrix while the selectivities were increased. As explained above, the permeabilities and selectivities of CMS membranes show the reasonable agreement about the relationship between the gas separation properties and final pyrolysis temperature. From the results, the CMS 500 showed O₂ permeability of 495 Barrers and O₂/N₂ selectivity of 11. At 700°C, the O₂/N₂ selectivity improved to 15 while the O₂ permeability decreased to 136 Barrers. Other CMS membranes (CMS 550-P55 and CMS 700-P55) show the same trends with regard to the final pyrolysis temperatures.

As shown in Fig 6, the CMS membranes derived from PI/PVP precursors show the higher permeabilities than CMS membranes prepared by pyrolysis of PI precursors about all gas molecules. From the results, the gas permeabilities of CMS membranes enhanced by PVP which provided the more interlayer spacing in the carbon matrix. Therefore, gas molecules permeate through the porous carbon structure in the carbon matrix. The O₂ permeability of CMS 550-P55 membranes were improved to 808 Barrers while the CMS 550 membranes showed O₂ permeability of 495 Barrers. For the CMS 700-P55, O₂ permeability increased as

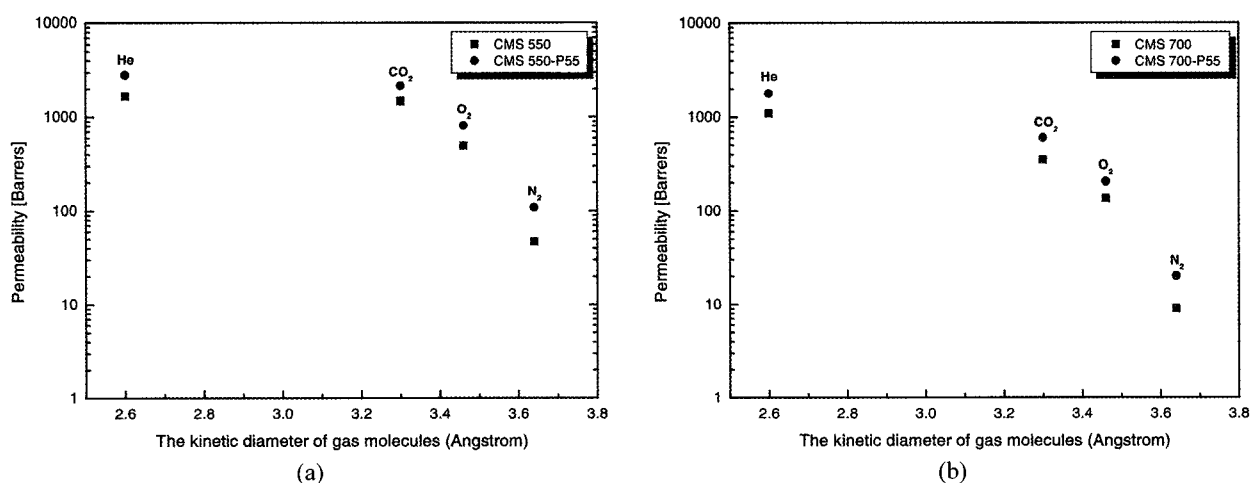
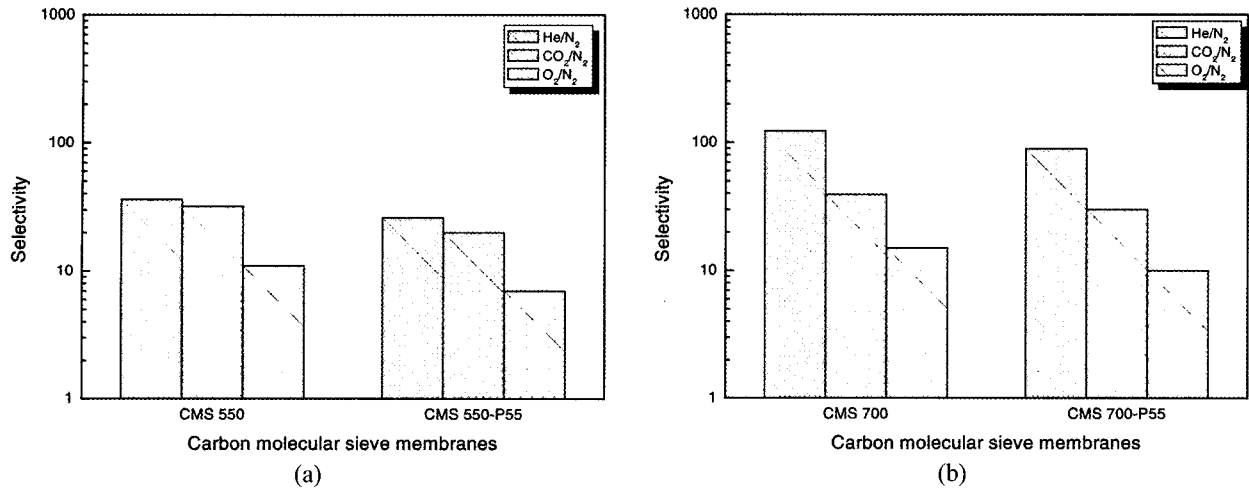
**Fig. 7.** Gas permeabilities of CMS membranes pyrolyzed at (a) 550 and (b) 700°C

Table 4. O₂ and N₂ Diffusion Coefficient and Diffusion Selectivities of CMS Membranes at 25°C

CMS membranes	Diffusion coefficient [1×10^{-8} cm ² /s]		Diffusion selectivity
	D(O ₂)	D(N ₂)	D(O ₂)/D(N ₂)
CMS 550	8.14	1.01	8.08
CMS 550-P55	16.24	2.66	6.17
CMS 700	1.42	0.13	10.92
CMS 700-P55	3.15	0.39	8.08

**Fig. 8.** Selectivities of CMS membranes pyrolyzed at (a) 550 and (b) 700°C

much as 69 Barrers compared with the CMS 700 membranes.

The selectivities depend on the final pyrolysis temperature and pyrolyzing polymer as shown in Fig. 8. Increasing the final pyrolysis temperature leads to reduced the effective pore sizes and the interlayer spacing in the carbon matrix. The selectivities of He/N₂, CO₂/N₂, and O₂/N₂ increased with increasing final pyrolysis temperature and were reduced by introducing PVP for the CMS membranes.

The diffusion coefficient and diffusion selectivities of O₂ and N₂ are reported in Table 4. Diffusion coefficient (D) can be estimated from the membrane thickness (L) and the time lag from a transient permeation measurement:

$$D = \frac{L^2}{6\theta} \quad (3)$$

Generally, dense polymeric membranes and molecular sieving media like zeolites and carbon molecular sieves (CMS) transport gas molecules by a similar sorption-

diffusion mechanism. Permeability ($P=D \times S$) can be expressed as the diffusion coefficient (D) and sorption coefficient (S). The permselectivity can be signified with the diffusion selectivity and sorption selectivity term. In the case of CMS membranes, the separation properties were remarkably determined by the diffusion selectivity term. The sorption selectivity term for O₂/N₂ is in the range of 0.7-2 for CMS membranes. In this study, the selectivity of CMS membranes derived from PI and PI/PVP precursors were determined mostly by the diffusion selectivity term in their gas separation.

Fig. 9 shows O₂ permeabilities versus O₂/N₂ selectivities of CMS membranes prepared in this study. CMS membranes prepared by pyrolyzed precursors containing the pyrolyzing polymer (PVP) have the potential to improve gas permeation property with a similar gas molecular size (O₂/N₂, and CO₂/N₂). Consequently, we can say that the pyrolyzing polymer leads to the formation of porous carbon structures in the carbon matrix and then acts as important component to improve the gas permeation property.

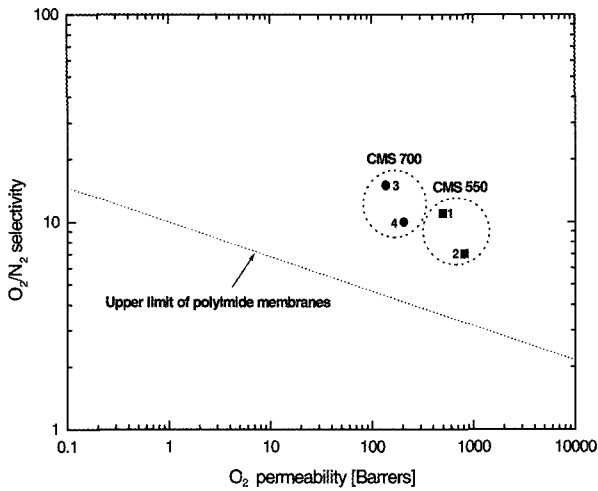


Fig. 9. O_2/N_2 selectivity versus O_2 permeability: 1=CMS 550, 2=CMS 550-P55, 3=CMS 700, and 4=CMS 700-P55.

4. Conclusion

In this study, we have prepared the CMS membranes derived from polyimide/polyvinylpyrrolidone blend precursors and investigated their characteristics and gas permeation properties. The structural changes of CMS membranes were caused by the different thermal properties of polymers and final pyrolysis temperatures. Introduced pyrolyzing polymer (PVP) led to the enhanced interlayer spacing and less compact porous carbon structures in the carbon matrix during the pyrolysis. The gas permeabilities of CMS membranes derived from PVP containing precursors were enhanced while their selectivities were less reduced. In addition, the final pyrolysis temperature affected the gas permselectivity of CMS membrane because of the reduced diffusion pathway of gas molecules. From the results, the CMS membrane (CMS 550-P55) prepared by introducing PVP showed the enhancement in gas permeability for O_2 by 63% while their O_2/N_2 selectivity was less reduced compared with CMS 550.

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