



Fabrication and characterization of PPO/PVP blend carbon molecular sieve membranes for H₂/N₂ and H₂/CH₄ separation

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ABSTRACT

Through a spin-coating technique, a high performance carbon molecular sieve (CMS) membranes were fabricated from thermally stable polymer polyphenylene oxide (PPO) and thermally labile polymer polyvinylpyrrolidone (PVP). The permeation results show that the small gas molecules (H₂, CO₂, N₂, and CH₄) transport mechanism is dominated by the molecular sieving effect. The permeation performances have a strong dependency upon polymer concentration and pyrolysis temperature. The best performance for hydrogen permeability obtained with PPO 15 PVP pyrolyzed at 700 °C was 1121 Barrer (1 Barrer = 1×10^{-10} cm³ (STP) cm/[cm² s cm Hg]) and the values of selectivity for gas pairs such as H₂/N₂ and H₂/CH₄ were 163.9 and 160.9, respectively. The correlation factor of permselectivity of H₂/N₂ and H₂/CH₄ gas pairs obtained from PPO and PPO/PVP derived CMS membranes were above the Robeson (2008) upper bound. The addition of thermally labile PVP creates diffusion pathways and controls selectivities for the CMS membranes derived from PPO 10 PVP and PPO 15 PVP.

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1. Introduction

In the last two to three decades, carbon molecular sieve (CMS) membranes have become one of the promising materials for gas separation. Many research groups have successfully fabricated CMS membranes for various applications such as hydrogen separation from gasification gas, purification of methane, separation of olefin/paraffin, and recovery of CO₂ and H₂O from natural gas [1,2]. Due to the increasing demand for high-performance CMS-based membranes, modifications of their synthesis procedure have been continuously evaluated in recent years. These include the use of inorganic additives [3,4], pyrolysis under different conditions [5], and post-treatment [6]. However, they still provided higher permeability with low selectivity performances and vice versa even obtained from complex procedure, and showed short comings with Robeson's upper bond line [7,8]. In an effort to strike a compromise between these extremes, scholars have focused on new polymeric precursors and investigated their effects on the structure and gas separation properties of the membrane.

Particular attention has been given to the polymer with high glass transition temperature, since it is associated with thermal stability of CMS membranes [9–14]. Generally, thermally stable

polymers tend to carbonize whereas thermally labile polymers easily decompose into gaseous products at high temperatures. Therefore, during pyrolysis, the use of thermally labile polymers as precursors may leave excessive amounts of pores in the carbon matrix. Ozaki et al. [15] first attempted the use of the thermally labile polymer, poly (vinyl butyral) (PVB), and studied its effects on the pore structures of CMS membrane. Other research groups also studied thermally labile polymers such as polyethylene glycol (PEG) [16–18] and investigated their use in fabrication of CMS membranes and their gas separation properties. Kim et al. [19] prepared carbon membranes from a blend containing thermally labile polyvinylpyrrolidone (PVP). They investigated the effect of blend ratio and phase separation behavior on the carbon structures and separation performance of CMS membranes [19]. They also examined the effect of PVP molecular weight on gas separation properties of CMS membranes derived from the polymer [20]. They found that these carbon membranes did not possess macro- or meso-pores. This is due to the micro-phase separation behavior during blending of the polymers.

Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) is one of the thermally stable polymers with the highest glass transition temperature. It has been used for preparing CMS membranes with high gas separation performance. Lee et al. [21] fabricated carbon membranes from PPO/PVP blends by preoxidation of the dip-coated polymer containing a low PPO/PVP concentration (3.0 wt.%) on the alumina ceramic support. This was followed by carbonization at 500–800 °C and cooling under Ar. The results indicated that with

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the PVP concentration decreasing to 0.6 wt.%, the gas permeability was decreased and the selectivity was increased due to reduction of pore volume and surface area of carbon membrane [21]. Lee et al. [22] continued their work on the PPO/PVP blend membrane and further discussed the effect of PVP molecular weight on the final carbon structure [22]. They found that blending with lower PVP molecular weight decreased permeability compared with CMS membranes derived from pure PPO. With higher PVP molecular weight, gas permeance increased and selectivity decreased due to the enhanced diffusional pathways in the polymer region. However, up to our knowledge, the effect of PPO concentration on PPO/PVP derived CMS membranes with low-molecular weight PVP and their gas permeation rates have not been reported.

The objective of this present work was to evaluate the effect of PPO concentration in PPO/PVP blends for fabrication of CMS membranes. In order to discuss the influence of thermal stability of PPO on the final pore structure of CMS membrane, the effect of pyrolysis temperatures were also investigated through H₂, CO₂, N₂, and CH₄ molecules permselectivity. All carbon membranes were characterized by field emission scanning electron microscopy (FE-SEM) and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials and membrane preparation

Pure precursor materials of poly (2,6-dimethyl-1,4-phenylene oxide) (PPO, molecular weight: 30,000 g/mol) and polyvinylpyrrolidone (PVP, molecular weight: 10,000 g/mol) were purchased from Aldrich Co., USA. The solvent chloroform was purchased from J.T. Baker Co., USA. The sample code of each PPO- and PPO/PVP blend-derived CMS membranes are presented in Table 1.

The polymer precursors were added to chloroform at fixed proportions and stirred thoroughly for 24 h to form homogeneous casting solutions. The casting solution was coated on the macroporous alumina disks support with spin coating technique at 2000 rpm 15 s for several times to get uniform thickness of polymer film. The disk support (porosity: 40–48%, average pore size: 0.14 μm, and diameter: 23 mm) was purchased from Ganya Fine Ceramics Co., Taiwan. After coating, all membranes were dried at room temperature for 24 h. Then, the resulting polymer membranes were pyrolyzed in the center of a quartz tube of a high temperature furnace (supplied from C.F. Electric heating Co., Taiwan) equipped with heating elements to minimize the axial and radial temperature gradients. A standard ANC-602 programmable temperature controller was used to control the precise temperature–time protocol. The tube was sealed using a glass stopper with an o-ring clamp for curing (preheated) in a heating furnace under vacuum at 240 °C for 6 h and a heating rate of 5 °C min^{−1} to remove excess solvent. After curing, the membranes were pyrolyzed at 400, 500, 600, and 700 °C under a vacuum system with a heating rate of 5 °C min^{−1}, and then held at the final temperature for 1 h. A standard pyrolysis temperature program was used to prepare the carbon membranes. Upon reaching room temperature, the resultant carbon membranes were removed from the furnace.

All CMS membranes were kept in a moisture buster to keep from moisture and dust until use. Samples were prepared based on each condition and subjected to the independent permeation test. The permeation values were the average [standard deviation (STDV)] of at least three independent measurements.

2.2. Gas permeation experiments

A standard vacuum time lag method was used to measure single-gas permeabilities at 25 °C. Feed pressures of 2 atm H₂ (0.289 nm), CO₂ (0.33 nm), N₂ (0.364 nm), and CH₄ (0.38 nm) were tested. The experimental set-up system has been illustrated in a previous study [23]. Leak detection tests were performed on all valves prior to the experiments. In addition, during each membrane change, the membrane was exposed to vacuum overnight prior to measurement until both the feed and the permeate sides of the membrane cell were evacuated to lower than 10^{−5} Torr. Pressure was measured using pressure transducers. Data were recorded using the VisiDag Builder software.

The permeability coefficients were determined by the following equation:

$$P = \frac{dp}{dt} \left(\frac{VT_0L}{p_0T\Delta pA} \right)$$

where P is the permeability expressed in Barrer [$1 \text{ Barrer} = 1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm}/(\text{cm}^2 \text{ s cmHg})$], dp/dt is the rate of pressure rise at steady state, V (cm³) is the calibrated downstream volume, L (cm) is the membrane thickness, Δp (cmHg) is the pressure difference between the feed side and the permeate side, T (K) is the measurement temperature, A (cm²) is the membrane effective area, and p_0 and T_0 are the standard pressure and temperature, respectively. Each sample was prepared at least three times with standard deviation (STDA). The ideal selectivity for gas A to gas B is defined by

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

2.3. Characterization of composite membrane

Weight loss of the polymer precursor during pyrolysis was characterized by a TGA Seiko SSC 5000 thermogravimetric analyzer. The analysis was carried out with a ramp of 10 °C min^{−1} at a temperature ranging from 50 to 800 °C. The pure gas N₂ and its flow rate were controlled at 50 ml min^{−1}. Likewise, surface morphologies of the prepared CMS membranes were investigated by SEM using an FE-SEM, JSM 5600 device.

3. Results and discussion

3.1. Characterization of CMS membranes

3.1.1. TGA analysis

Thermal decomposition behaviors of thermally stable polymer PPO, thermally labile polymer PVP, and PPO/PVP polymer blends

Table 1
Preparation of the different sample code concentrations (wt.%) in the polymer of PPO and blends of PPO/PVP in chloroform.

Sample code	Total sample code concentration (wt.%)	Thermally stable polymer (PPO)		Thermally labile polymer (PVP)	
		Concentration of the polymer (wt.%)	Weight of the polymer (g)	Concentration of the polymer (wt.%)	Weight of the polymer (g)
PPO 10	10	10	2.0	–	0
PPO 15	15	15	3.0	–	0
PPO 10 PVP	10	7.5	1.6	2.5	0.4
PPO 15 PVP	15	12.5	2.4	2.5	0.6

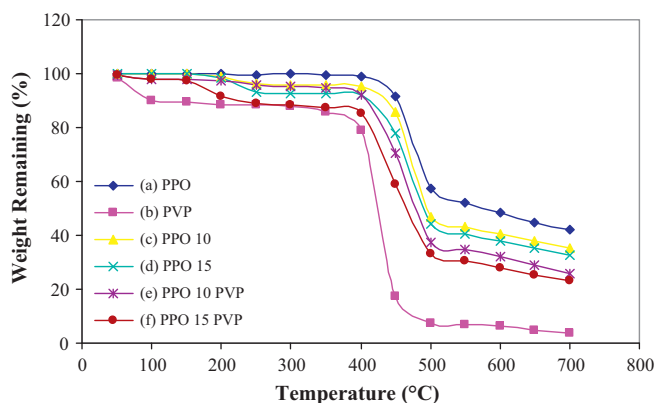


Fig. 1. TGA curves for the pure polymers: (a) PPO; (b) PVP and different wt.% polymers: (c) PPO 10; (d) PPO 15; (e) PPO 10 PVP; (f) PPO 15 PVP.

were observed during heating up to 800 °C under a nitrogen flow using a standard temperature program. As illustrated in Fig. 1, the thermally stable polymer PPO (a) was stable up to approximately 430 °C, and then degradation began between 430 and 500 °C. The thermally labile polymer PVP (b) started to decompose at temperatures around 380 °C. The total weight loss of PVP was measured to be above 90% at 600 °C [20,22,24]. Fig. 1(b) clearly displays the weight remaining for PVP at 600 °C as less than 10%. From Fig. 1, PPO 10 (c) shows the weight remaining at 600 °C as slightly higher than that of PPO 15 (d). This behavior might be due to the early loss of chloroform present in the polymer matrix.

The polymer blend PPO 10 PVP (e) is a thermally stable polymer that decomposed polymer structures at 420 °C, a value lower than

that of pure PPO. Similar trends were also observed for PPO 15 PVP (f), which decomposed at approximately 410 °C, also lower than that of PPO 10 PVP. At temperature around 700 °C, thermally stable polymers, such as pure PPO, PPO 10, and PPO 15, showed slightly higher weight remaining compared to PPO/PVP blend-based membranes. This could be attributed to the addition of PVP. For each concentration of the thermally stable polymers PPO 10 and PPO 15, a slight variation in final weight remained at 700 °C, likely due to the solvent concentration present in PPO. A similar behavior was evident in PPO 10 PVP and PPO 15 PVP-based membranes due to the addition of PVP and the early loss of solvents present in the membranes.

3.1.2. FE-SEM of CMS membranes

Fig. 2(a) and (b) depicts the cross-sectional FE-SEM images of the PPO 10 PVP membranes pyrolyzed at 600 °C and 700 °C, respectively. As shown, in the porous structure in the cross section of PPO-based CMS membrane modified with PVP were enhanced with pyrolyzed temperature increased to 700 °C, and the porous structure could be found in the most part of cross section. With the increase in pyrolyzed temperature from 600 to 700 °C, some small close voids appeared close to the end of original porous structure, and original voids developed further and become wider. According to the changes of the cross section morphology, the presence of a few percentage of PVP was sufficient to induce the formation of porous structure. In general, PVP polymer has low thermal stability compared to PPO, during the pyrolysis stage, PVP polymer undergo carbonization quickly [22] and create voids in the PVP phase region. The whole process for the voids formation is schemed in Fig. 3. These voids will allow the gas molecules pass rapidly and increase the permeability of the membrane. Further, the car-

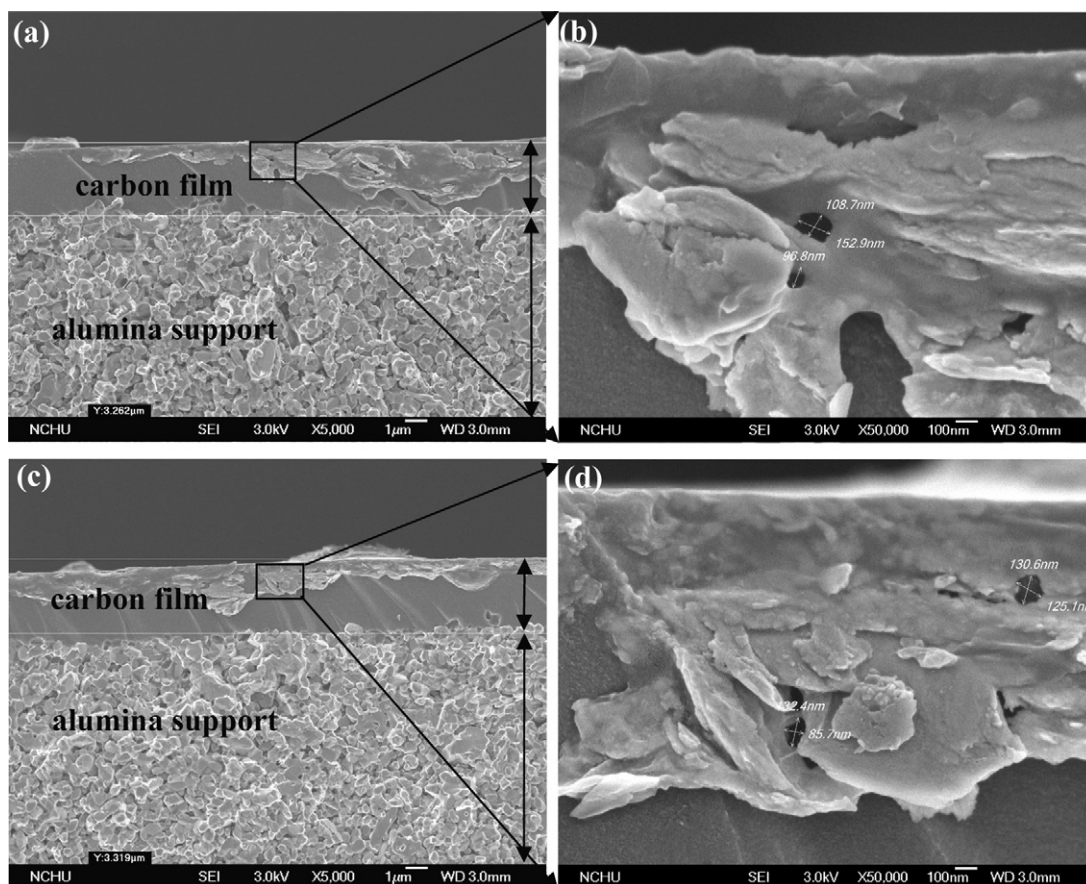


Fig. 2. FE-SEM images of PPO blend with PVP based carbon membranes: (a) cross-section view of PPO 10 PVP at 600 °C; (b) higher magnification part of (a); (c) cross-section view of PPO 10 PVP at 700 °C; (d) higher magnification part of (c).

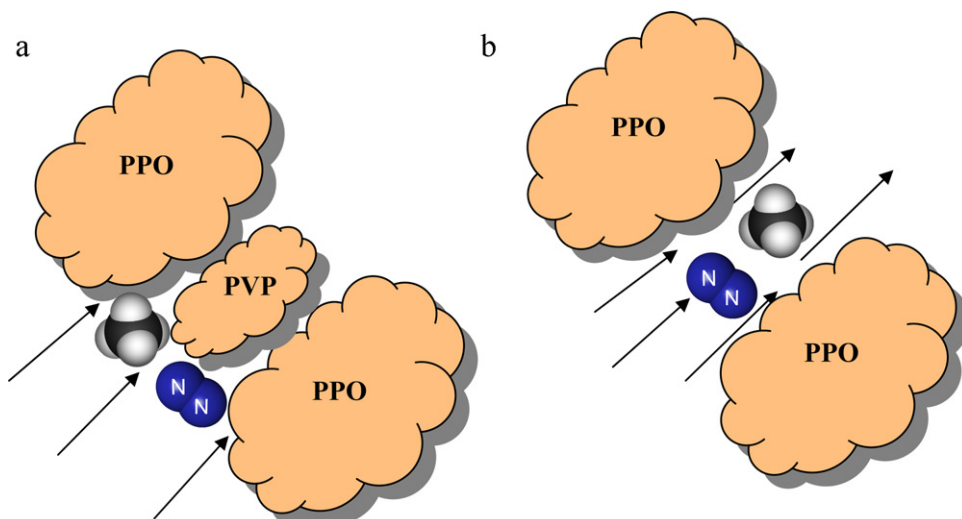


Fig. 3. PPO/PVP blend based membranes diffusional pathways: (a) before pyrolysis, (b) after pyrolysis.

bon film layer was approximately $3.2 \pm 0.4 \mu\text{m}$ thick. An excellent adherence between the porous carbon matrix film layer and the macro-porous alumina support was observed, confirming that the multiple-times coating of polymeric films on the surface of macro-porous alumina support could form an excellent carbon film after pyrolysis.

3.2. Effect of pyrolysis temperature on the gas permeation properties of CMS membranes

3.2.1. PPO-based CMS membranes

Gas permeation properties of pure PPO-based CMS membranes were evaluated through single-gas permeation experiments. Fig. 4 shows the gas permeation performances for carbon membranes prepared from PPO at different pyrolysis temperatures. The carbon membranes prepared at 600 and 700 °C showed high performances for all examined gas species. As the permeance for gas species shows, permeation rates through the carbon membranes were correlated with the kinetic diameter of gas species. Fig. 4(a) shows that H_2 permeability dramatically increased with increasing pyrolysis temperature. A similar behavior is also evident in Fig. 4(b), showing that CO_2 permeability also increased with increasing pyrolysis temperature. Gas permeability decreased with the increase of molecular size. Gas transport is controlled by the molecular sieving effect in permeation results, especially for carbon membranes prepared at higher temperatures [20]. Fig. 4(c) and (d) shows that the permeabilities of N_2 and CH_4 decreased with increasing pyrolysis temperature. At pyrolysis temperatures of 600 and 700 °C, the shrinkage of pore structures from the molecular sieving-controlled transport of gas species caused a decrease in permeances.

Fig. 5 illustrates the effect of pyrolysis temperature on selectivity for various gas combinations in PPO-based carbon membranes. Fig. 5(a) illustrates that H_2/N_2 permselectivity increased with increasing pyrolysis temperature. A similar behavior was evident with H_2/CH_4 selectivity, which also increased with increasing pyrolysis temperature. As the figure shows, in carbon membranes at a low temperature (400 °C), the permselectivity for H_2/N_2 and H_2/CH_4 were 18.43 and 18.46, respectively. However, the values increased to 43.02 and 43.06 in the permeation of PPO-based carbon membranes prepared at 700 °C due to the shrinkage of pore structures formed on the carbon film. The effect of pore structure shrinkage on H_2/N_2 and H_2/CH_4 selectivity can be clearly observed in Fig. 5(a) and (b) at 700 °C. The selectivities of CO_2/N_2 and CO_2/CH_4 at higher pyrolysis temperatures (600 and 700 °C)

were shown to decrease due to the decrease in CO_2 permeance [Fig. 4(b)]. The values for CO_2/N_2 and CO_2/CH_4 were between 5 and 11 at lower temperatures (400 and 500 °C). The permeation results for carbon membranes prepared at 600 and 700 °C show slightly decreased values for CO_2/N_2 and CO_2/CH_4 between 11 and 10 due to the shrinkage of pore structures. Based on the permeation results, pyrolysis at 700 °C displayed the highest gas permeation performance for the fabrication of CMS membranes derived from PPO-based membranes [9]. Therefore, carbon membranes prepared at 700 °C show lower permselectivity than carbon membranes prepared at lower temperatures. The permeation performance for PPO-based carbon membranes were best in structures developed at 500 and 600 °C.

3.2.2. PPO/PVP-based CMS membranes

PPO/PVP-based CMS membranes were prepared at different pyrolysis temperatures to investigate the influence of PVP and pyrolysis temperatures on gas permeation rates. Fig. 6 represents the effect of pyrolysis temperature on various gas permeations in PPO/PVP-based CMS membranes. As shown in Fig. 6(a) and (b), carbon membranes prepared at 600 and 700 °C had high permeances for all examined gas species. For H_2 and CO_2 , permeability increased with increasing pyrolysis temperature; the pore structure may have enlarged due to the voids occupied by PVP [5], enabling small kinetic gas molecules to pass into the nano-pore channels in the CMS membranes. The permeation results of N_2 and CH_4 in Fig. 6(c) and (d) show decreased values for carbon membranes prepared at 600 and 700 °C. Therefore, the addition of PVP changed the carbon pore structure, especially at higher temperatures. This effect was most evident in the gas permeation rate performances derived from PPO/PVP-based CMS membrane structures developed at 700 °C. The single-gas permeation results of all CMS membranes show that gas transport was controlled by the molecular sieving mechanism, suggesting that CMS membranes prepared with high PPO concentrations (PPO 15 PVP) provided an enhanced diffusion path for the gas species in the PVP domain [19,20].

The effect of pyrolysis temperature on the performance of CMS membrane permselectivity for various gas pairs at different pyrolysis temperatures are shown in Fig. 7. Fig. 7(a) and (b) displays the gas pairs H_2/N_2 and H_2/CH_4 for various pyrolysis temperatures on the performance of carbon membranes. At a low pyrolysis temperature (400 °C), the selectivities of H_2/N_2 and H_2/CH_4 were 27.55 and 27.88, respectively [Fig. 7(a) and (b)]. For higher temperatures, the gas permeation rates for carbon membranes prepared at 700 °C

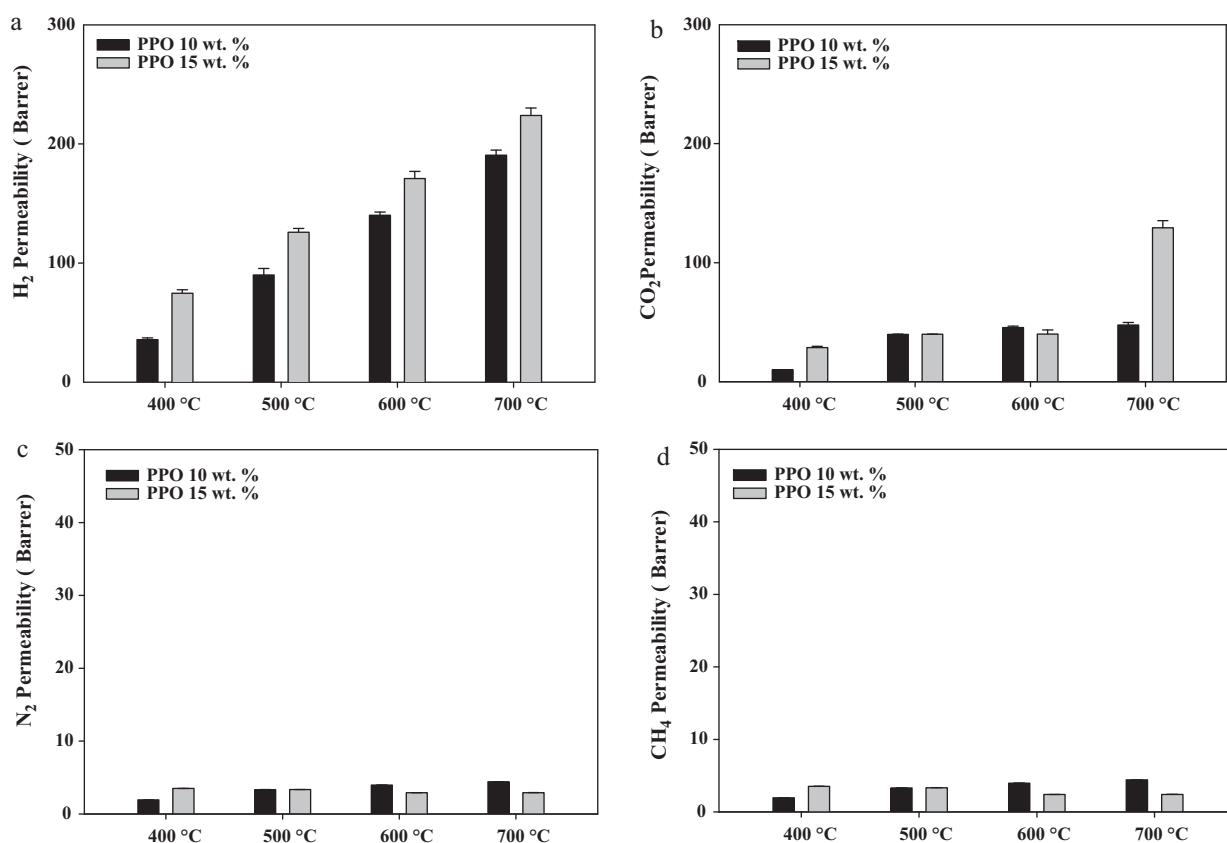


Fig. 4. Effects of polymer concentration and pyrolysis temperature on (a) H₂, (b) CO₂, (c) N₂ and (d) CH₄ permeabilities of PPO based CMS membranes.

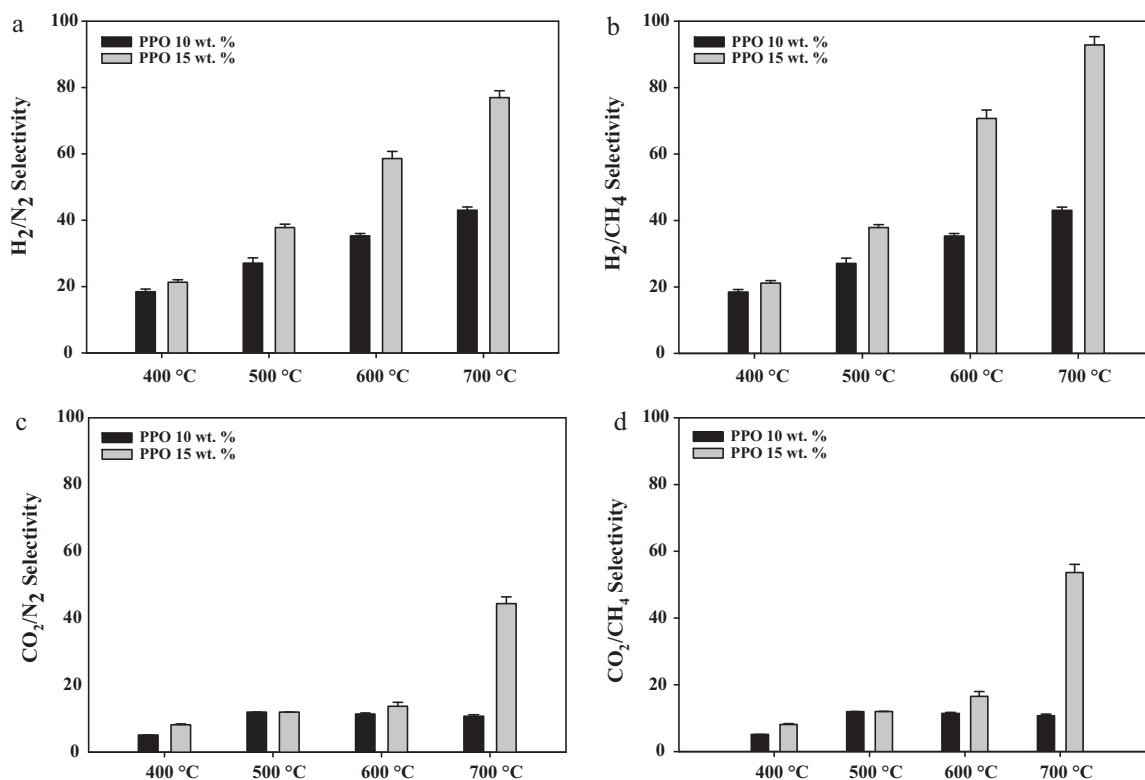


Fig. 5. Effects of polymer concentration and pyrolysis temperature on (a) H₂/N₂, (b) H₂/CH₄, (c) CO₂/N₂ and (d) CO₂/CH₄ selectivities of PPO based CMS membranes.

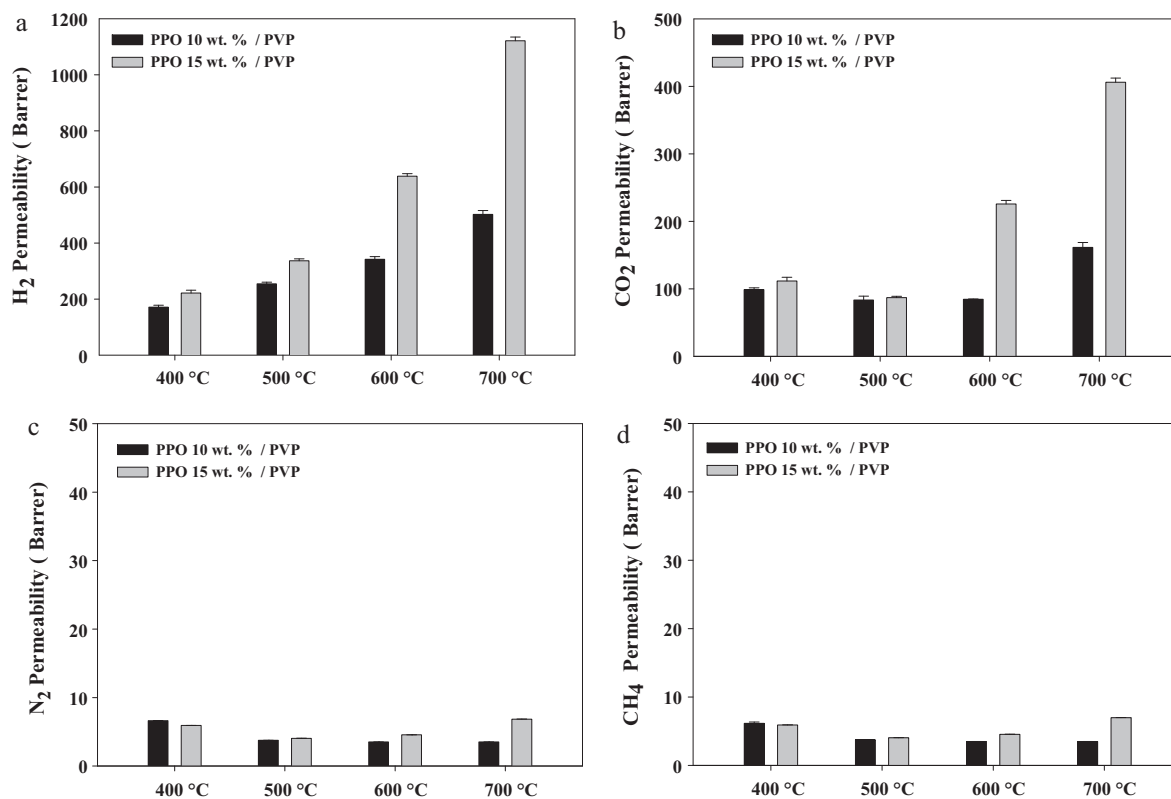


Fig. 6. Effects of polymer wt.% loading and pyrolysis temperature on (a) H₂, (b) CO₂, (c) N₂ and (d) CH₄ permeabilities of PPO/PVP based CMS membranes with different pyrolysis temperatures.

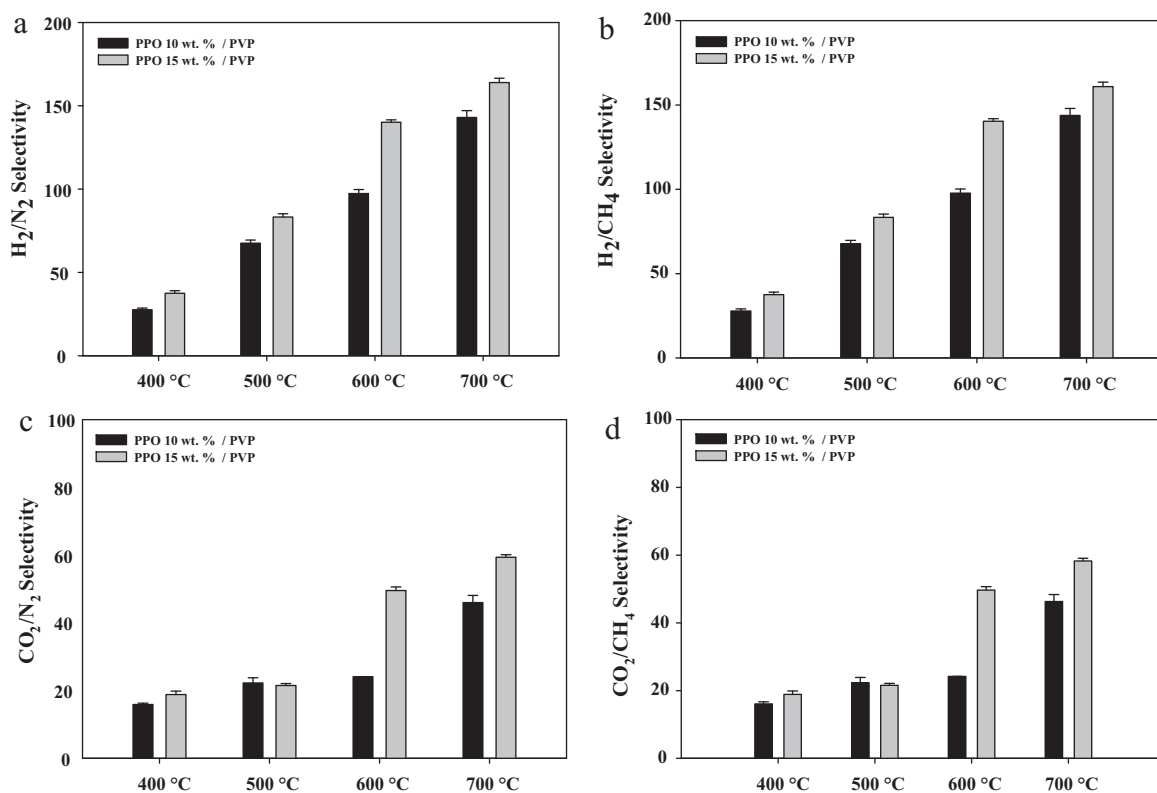


Fig. 7. Effects of polymer wt.% loading and pyrolysis temperature on (a) H₂/N₂, (b) H₂/CH₄, (c) CO₂/N₂ and (d) CO₂/CH₄ selectivities of PPO/PVP based CMS membranes with different pyrolysis temperatures.

drastically increased from 27.55 (400 °C) to 143.00 for H₂/N₂ and from 27.88 (400 °C) to 143.80 for H₂/CH₄. Notably, the selectivities for CO₂/N₂ and CO₂/CH₄ increased from 15.89 at lower temperatures (400 °C) to 46 at higher temperatures (700 °C), and from 16.08 at lower temperatures (400 °C) to 46.26 at higher temperatures (700 °C), respectively. Fig. 7(c) and (d) shows the CO₂/N₂ and CO₂/CH₄ selectivities for PPO/PVP-based CMS membranes. The selectivities increased along with increasing pyrolysis temperatures from 400 to 700 °C. This may be due to the characteristic pore properties, which decrease at high pyrolysis temperatures [9]. The pyrolysis temperature effect on CMS membrane performance confirms that the carbon membranes prepared with higher temperatures have decreased pore structures [21,22]. Considering the permselectivity of CO₂ with gas species of larger kinetic diameters (N₂ and CH₄), the experimental results show significant improvement for carbon membranes prepared at higher temperatures (600 and 700 °C) than at lower temperatures (400 and 500 °C). This might be caused by the addition of PVP, which decreased the pore structure of the CMS membrane and led to better CO₂ permeance at higher temperatures.

3.3. Effect of polymer concentration (wt.% loading) on the gas permeation properties of CMS membranes

3.3.1. PPO-based CMS membranes

The influence of PPO concentration (wt.%) on permeation performance was investigated for the CMS membranes derived from PPO 10 wt.% and PPO 15 wt.%. Fig. 4 presents the permeance of gas species for carbon membranes derived from PPO 10 and PPO 15 at permeation temperature 25 °C. The results were compared with those at different pyrolysis temperatures. For all carbon membranes, the permeation results show that gas transport was controlled by the molecular sieving mechanism. Generally, the permeabilities of small gas species through micro-porous membranes, such as carbon membranes, are concomitant with the order of kinetic diameter of the gas species. The carbon membranes derived from the PPO with lower concentration (PPO 10) than PPO 15 show increased permeances with increasing pyrolysis temperature. Notably, the gas permeance increased in carbon membranes derived from PPO 15, which has micro-porous structures and smaller characteristic values than PPO 10 carbon membranes.

Fig. 5 illustrates the effect of polymer wt.% loading on different gas pair selectivities of PPO-based CMS membranes. Fig. 4(a) and (b) shows that the selectivities for H₂/N₂ and H₂/CH₄ increased with increasing polymer wt.% loading from PPO 10 to PPO 15. This may be due to the weight remaining on the final temperature for PPO 10 and PPO 15 (Fig. 1). The shrinkage of pore structures in the final carbon films depends on early evaporation of the solvent in the membranes. For polymers, permanent gases that permeate through the micro-pore channels are called free volumes. These micro-pore channels are very small; thus, fluctuations due to thermally induced vibrations [depending on polymer concentration (wt.%)] significantly affect the average pore size and permselectivity [25,26]. The values of CO₂/N₂ and CO₂/CH₄ were between 10.72 to 44.41 and 10.73 to 53.31, respectively, at temperatures from 400 to 700 °C [Fig. 5(c) and (d)]. The permeation results for CMS membranes prepared at 600 and 700 °C significantly decreased for PPO 10-based membranes, but increased for PPO 15-based membranes along with increasing pyrolysis temperature and wt.% loading of the polymer.

3.3.2. PPO/PVP-based CMS membranes

The permeances of gas species for CMS membranes derived from PPO/PVP blends with different PPO concentrations were compared to that of pure PPO-based CMS membranes at different pyrolysis temperatures (Fig. 6). The permeation results of all CMS membranes show that gas transport was controlled by the molecular

sieving mechanism for carbon membranes prepared in lower concentrations of PPO 10 PVP compared to those prepared at higher concentrations (PPO 15 PVP). CMS membranes prepared with PPO 15 PVP provide an enhanced diffusion pathway for gas species in the domain of PVP [19,20]. Fig. 6(a) and (b) shows increase in the gas permeance of H₂ and CO₂ for CMS membranes at different pyrolysis temperatures and wt.% loading of PPO. The permeances of N₂ and CH₄ slightly decreased for CMS membranes prepared with PPO 10 PVP. The permeation results imply that the addition of PVP at different wt.% loading of PPO concentrations decreased the permeance for N₂ and CH₄ [Fig. 6(c) and (d)]. However, the CMS membranes of PPO 15 PVP at 600 and 700 °C show slightly increased permeance values for N₂ and CH₄. The addition of PVP with high wt.% loading of PPO 15 PVP caused the permeances to notably increase approximately five times more in a high pyrolysis temperature (700 °C) than at a low pyrolysis temperatures (400 °C). A similar behavior was displayed with PPO 10 PVP from low pyrolysis temperatures to high pyrolysis temperatures.

Fig. 7 demonstrates the effect of polymer wt.% loading on H₂/N₂, H₂/CH₄, CO₂/N₂, and CO₂/CH₄ selectivities for PPO/PVP-based CMS membranes with different pyrolysis temperatures. In the permselectivity of H₂/N₂ and H₂/CH₄, as shown in Fig. 7(a) and (b), respectively, the estimated value increased with increasing wt.% loading of PPO with increased pyrolysis temperature. The permselectivity value of H₂/N₂ for the PVP 15 PVP CMS membrane at low temperature (400 °C) was approximately 37.43; at higher temperature (700 °C) the value increased approximately four times (~163.90). This effect was likely caused by the addition of PVP and increased wt.% loading of PPO. Higher separation factors than those expected from Knudsen diffusion were achieved, confirming that the pores of fabricated CMS membranes are of molecular dimensions. Fig. 7(c) and (d) shows the separation factors of CO₂/N₂ and CO₂/CH₄ with different pyrolysis temperatures with increasing wt.% loading of the polymer. Based on the permselectivity of CO₂ with gas species having larger kinetic diameter (N₂ and CH₄), the estimation results show significantly higher values compared with the carbon membranes of PPO 10 PVP at lower temperatures. The permselectivity of CO₂/CH₄ in Fig. 7(d) was 18.83 for PPO 15 PVP-derived carbon membrane at 400 °C; subsequently, selectivity increased as pyrolysis temperature increased. The results presented in Table 2 belongs to various carbon membranes for gas separation applications reported in the literature [23,27–32]. The present PPO/PVP based CMS membranes have superior performance compared to the other synthesized membranes.

3.4. Correlation of permeability and permselectivity for PPO and PPO/PVP-based CMS membranes

Fig. 8 shows the trade-off among H₂ permeability, H₂/N₂ permselectivity, and H₂/CH₄ permselectivity of PPO and PPO/PVP-based CMS membranes with different polymer concentrations. Based on permeation results, the relationship between permeability and permselectivity was considered for the CMS membranes derived from PPO and PPO/PVP-based membranes pyrolyzed at 700 °C. Fig. 8(a) presents the correlation of permeability and permselectivity for the H₂/N₂ with the Robeson upper bound line and revisited upper bound line [7,8]. The H₂ permeability and the permselectivity show higher permeation performance compared with the Robeson upper bound and revisited upper bound limit for polymer membranes. The permeation results of PPO 10 and PPO 15 were within the range of 190–223 Barrer, slightly above the Robeson (1991) upper bound line and the Robeson (2008) upper bound line. In contrast, those of PPO 10 PVP- and PPO 15 PVP-based carbon membranes pyrolyzed at 700 °C were much higher than the Robeson (2008) revisited upper bound line compared to PPO 10- and PPO 15-based CMS membranes. The addition of thermally labile

Table 2
Comparison of permeation performance of the CMS membranes.

Type of membrane	Pyrolysis temperature (°C)	Permeation temperature (°C)	Permeability (Barrer)			Selectivity		Reference
			H ₂	N ₂	CH ₄	H ₂ /N ₂	H ₂ /CH ₄	
PEI ^a	600	25	384	157	–	2.4	1.7	[22]
PF resin ^b	800	20	51.2	1.6	1.7	30.4	29.0	[27]
PPESK ^c	650	30	758	19.4	–	39.1	–	[28]
PPESK ^c	650	30	118	0.68	–	174.1	–	[29]
TMSPPPO ^d	650	25	1843	12.4	–	148	–	[30]
PR ^e	600	35	51.7	1.8	1.3	28	37	[31]
PPESK ^c	650	25	1016	13.9	–	73.1	–	[32]
PPO 15 PVP	700	25	1121	6.8	6.9	163	160	This work

^a Polyetherimide (PEI).

^b Phenol formaldehyde resin (PF).

^c Poly (phthalazinone ether sulfone ketone) (PPESK).

^d Trimethylsilyl-polyphenylene oxide (PPO).

^e Phenolic resin.

polymer enhanced permeation performance by increasing the pore structure for the fabrication of CMS membranes for gas separations.

Fig. 8(b) represents the trade-off between H₂ permeability and H₂/CH₄ permselectivity in the CMS membranes together with the Robeson lines [7,8]. In this study, CMS membranes were successfully fabricated by adding thermally labile polymer PVP with thermally stable polymer PPO with different wt.% loadings of PPO at 700 °C. The PPO/PVP blend membranes and their performance improved compared with pure PPO-based CMS membranes. The CMS membranes derived from PPO containing a thermally labile polymer, which exhibited nano-phase channel separation performance, were superior candidate materials for improving gas separation performance. The values for PPO 10 PVP- and PPO 15 PVP-based carbon membranes pyrolyzed at 700 °C were much higher than the Robeson (2008) upper bound line compared with

the PPO 10- and PPO 15-based CMS membranes for H₂/CH₄ separation performance. In addition, all PPO/PVP-based membranes exceeded the Robeson (2008) revisited upper bound line for conventional polymeric membranes compared to PPO-based CMS membranes.

4. Conclusions

By blending thermally labile PVP polymer, it was possible to produce PPO/PVP blend CMS membranes with a high permselectivity performance due to a porous structure. The results of this study indicate that PPO and PVP concentration, pyrolysis temperature all played important roles in the formation of finally structure of CMS membrane. The carbon membranes prepared at 600 and 700 °C showed high performances for all examined gas species. As the permeance for gas species illustrated, the permeation rates through the carbon membranes were correlated with the kinetic diameter of gas species and have the excellent ability to separate smaller gases (H₂ and CO₂) from the bigger gases (N₂ and CH₄). Further, the pore structure has enlarged due to the voids created by decomposition of PVP under higher pyrolysis temperature. The development of porous structure enabled the small kinetic gas molecules to pass into the nano-pore channels in the CMS membranes. The permeation results imply that the addition of PVP with high wt.% loading of PPO 15 PVP caused the permeances to notably increase approximately five times more in a high pyrolysis temperature (700 °C) than at a low pyrolysis temperatures (400 °C).

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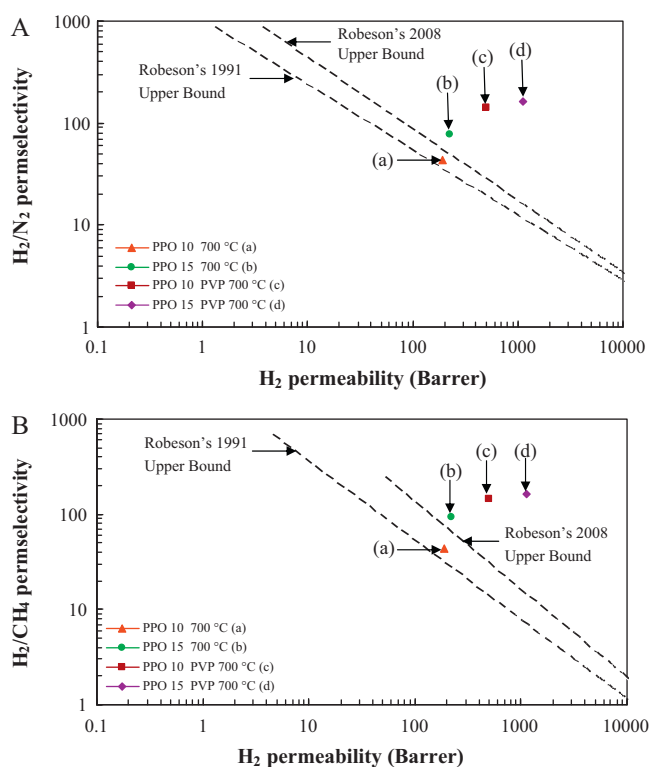


Fig. 8. Trade-off relationship between (A) H₂ permeability and H₂/N₂ permselectivity and (B) H₂ permeability and H₂/CH₄ permselectivity of PPO and PPO/PVP based carbon membranes with different wt.% loadings of polymeric concentration with same pyrolysis temperatures.

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