SEPARATIONS: MATERIALS, DEVICES, AND PROCESSES

Fabrication and Characterization of PEI/PVP-Based Carbon Hollow Fiber Membranes for CO_2/CH_4 and CO_2/N_2 Separation

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Carbon hollow fiber membranes derived from polymer blend of polyetherimide and polyvinylpyrrolidone (PVP) were extensively prepared through stabilization under air atmosphere followed by carbonization under N_2 atmosphere. The effects of the PVP compositions on the thermal behavior, structure, and gas permeation properties were investigated thoroughly by means of differential scanning calorimetry, thermogravimetric analysis, X-ray diffraction, and pure gas permeation apparatus. The experimental results indicate that the transport mechanism of small gas molecules of N_2, CO_2, and CH_4 is dominated by the molecular sieving effect. The gas permeation properties of the prepared carbon membranes have a strong dependency on PVP composition. The carbon membranes prepared from polymer blends with 6 wt % PVP demonstrated the highest CO_2/CH_4 and CO_2/N_2 selectivities of 55.33 and 41.50, respectively. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 3167–3175, 2012

Keywords: carbon membrane, polyetherimide, polymer blends, carbon dioxide, separation

Introduction

The emissions of carbon dioxide (CO_2), which is a major contributor to global warming, have been dramatically increased over the last 50 years and are still increasing each year.[1,2] Currently, capture of CO_2 with amine solvents is the most mature technology. Such systems, even though widely adopted, can pose operational difficulties due to the problems involved in keeping the solvent clean and operating within the process constraints of the system.[3] Thus, gas separation using membrane is the alternative possible contender and has been commercially used in a number of industrial processes since 1980. Nowadays, most of membrane processes are applied toward CO_2 removal. Carbon membrane is one of the new emerging materials that have been extensively studied for gas separation application. From literature, it is found that carbon membranes can be prepared from a wide range of polymeric precursors such as polyimides (PIs), polyetherimide (PEI), phenolic resin, polyfurfuryl alcohol, polyphenylene oxide (PPO), poly(vinylidene chloride-*co*-vinyl chloride), polyacrylonitrile (PAN), and phenol formaldehyde resin.[4–6]

Recently, the development of carbon membrane separation using polymer blend materials as a starting material has became popular and significant. It is indicated by a number of research works published in various international journals. It is generally known that the structure and gas permeation properties of carbon membrane can be modified by the post-treatment methods such as postpyrolysis, postoxidation, and chemical vapor deposition.[4–9] Besides these processes, modification can also be conducted during precursor membrane preparation. Modification of precursor membranes through polymer blending is one of the most cost effective and simple methods in tailoring the structure and properties of the resultant materials. An early work regarding the use of polymer blend as a carbon material precursor was disclosed by Ozaki et al. in 1997.[10] In recent years, several carbon membranes fabricated from other polymer blends have also been reported. Those include blending of PPO/polyvinylpyrrolidone (PVP),[9] PEI/PVP,[11,12] PAN/polyethylene glycol (PEG),[7] PAN/PVP,[7] PI/PEG,[13] PI/PVP,[8,14] phenol formaldehyde novolac resin/PEG,[15] and polybenzimidazole/PI.[16] Kim et al.[8] fabricated carbon membrane from PI/PVP blends by varying the heat-treatment conditions. Experimental results show that the gas permeability through the carbon membranes was enhanced by the introduction of thermally labile polymer, PVP. It is believed that the introduction of the thermally labile polymer could control the pore structure of carbon membrane. Separately, study on carbon membrane preparation from PPO and PPO/PVP precursor has also been carried out by Lee's group.[9,17–20] Coutinho et al.[11] on the other hand fabricated carbon membrane via pyrolysis of PEI/PVP hollow fiber membranes and studied the influence of heat-treatment conditions on the final membrane morphology

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Table 1. Preparation of PEI/PVP Precursor Membranes at Different PVP Compositions

Sample Code	PEI Concentration (wt %)	PVP Concentration (wt %)	Total Polymer Concentration (wt %)
PEI/0	17	0	17
PEI/6	17	6	23
PEI/8	17	8	25
PEI/10	17	10	27

using a statistical experimental design. Another relevance literature has been reported by Rao et al.,[12] who prepared PEI/PVP-based carbon membranes by spin coating technique using porous alumina disk as support. A more extensive literature summary on carbon membranes derived from polymeric materials for gas separation applications can be found in our review paper.[6]

Most of the research on carbon membrane for gas separation has been performed in flat sheet-supported membranes. There are few scientific paper works dealing with the gas permeation properties through asymmetric hollow fiber membranes at high feed pressures. Based on experimental results reported in the literature,[21] it is found that membranes with thin skin layer may show different physicochemical properties and permeation characteristics when compared with the respective thick film membranes prepared from the same material. In this work, the investigation on the preparation of carbon membrane derived from polymer blend of two types of polymer having different thermal properties has been undertaken in an effort to augment the current studies in carbon membrane for CO_2 separation. To the best of our knowledge, there were very few investigations on the application of carbon hollow fiber membrane-based PEI/PVP for gas separation. The study on the effects of the polymer composition on the carbon membrane performance is also rarely reported. Thus, this study seeks to demonstrate an ability to adapt the blending of polymer precursor method for attractive separation performance in CO_2 separation.

Materials and Experimental

Materials and membrane preparation

In this article, PEI (Ultem 1000) as the basic polymer and PVP (Fluka, K90) as the second polymer were used for making the blend membrane. Both polymers were dried overnight at 393 K prior use. The chemical N-methyl-2-pyrrolidone (NMP) with analytical grade was used as solvent without any purification. The composition of PVP used in this experiment was in the range of 6–10 wt % as presented in Table 1. A polymer solution was prepared by dissolving PVP in NMP solvent at 353 K until a homogeneous clear solution was formed. It was followed by adding PEI into the mixture. The hollow fiber membranes were then fabricated by a simple dry/wet spinning technique and the details of methods used in dry/wet spinning process have been described elsewhere.[22,23] The hollow fiber membranes were subjected to a simple solvent exchange process by immersing it into ethanol and n-hexane for 2 h each, followed by drying naturally for 1 day at room-temperature. Finally, the polymeric hollow fiber membranes were ready for heat treatment and testing.

The heat-treatment process was carried out by placing the precursor membrane at the center of Carbolite (Model CTF 12/65/550) wire-wound tube furnace with Eurotherm 2416CC temperature control systems. In the first step, the precursors were heated to 573 K under compressed air flow of 3.33×10^{-6} m^3/s with a heating rate of 0.05 K/s. This process was held for 1800 s to complete stabilization. In second step, the temperature was increased to carbonization temperature of 923 K with the same heating rate and held for 1800 s under N_2 flow of 3.33×10^{-6} m^3/s. At last, the furnace was allowed to cool gradually to room-temperature.

Membrane characterization

The glass transition temperatures (T_gs) of polymer blends and their compatibility were measured by a means of Mettler Toledo differential scanning calorimetry (DSC 822e). The thermal decomposition behavior of these polymers during heat-treatment process was characterized by Mettler Toledo thermogravimetric analyzer (TGA TSO800GC1) in flowing N_2 at a ramp of 0.17 K/s from 323 to 1173 K. The morphological structure of the precursor and carbon hollow fiber membrane was observed under JEOL JSM-5610LV scanning electron microscopy (SEM). The microstructure properties of resulting carbon membranes were examined on X'Pert PRO X-ray diffractometer (XRD) from PANalytical with the diffraction angle 2θ from 10° to 50°. Ni-filtered CuKα radiation with a wavelength of $\lambda = 1.54$ Å was applied in the experiments. The interplanar distance (d-spacing) of the carbon membranes were calculated by the well-known Bragg equation, as follows

$$n\lambda = 2d \sin \theta \tag{1}$$

where d is the dimension spacing (Å), θ is the diffraction angle (°), λ is the X-ray wavelength (Å), and n is an integral number (1, 2, 3, …).

Gas permeation measurement

An entire membrane module, 0.1 m length, composed of six hollow fibers was used. The calculated membrane area for transport in this module is approximately 2.1×10^{-3} m^2. The carbon membrane module was supplied as shell module, where the gases enter in the shell side, and the permeate exits through the bore side of the membranes. From gas permeation test, the performance of the carbon membranes can be characterized by two important parameters: permeance and selectivity. Simple soap film flow meter was used to obtain the permeation properties of the gas owing to its suitability for the measurement of small and wide range of flow rate.[24] The following gases were chosen as those with the potential for separation: CO_2, N_2, and CH_4. The permeance was determined in the sequence of N_2, CH_4, and CO_2 at room-temperature and 700 kPa. Each measurement value is the result of three different membranes and the precision in gas permeance for each membrane was found to be within the error range of ±10%. The permeance, P (GPU) and selectivity, α of the membranes were calculated using the following equations

Permeance, P (GPU)

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{\Delta p \cdot A} = \frac{Q}{n\pi D l \Delta p} \tag{2}$$

$$1 \text{ GPU} = 1 \times 10^{-6} \text{cm}^3(\text{STP})/\text{cm}^2 \text{ s cm Hg}$$

Selectivity, α

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \tag{3}$$

Table 2. Thermal Analysis Data of PVP, PEI, and Polymer Blends of PEI/PVP

Polymer Blends	T_g (K)	T_d (K)	Char Yield (%)
PVP	453 ± 1	643 ± 1	15 ± 1
PEI/0	493 ± 1	833 ± 1	50 ± 1
PEI/6	489 ± 1	703 ± 1	47 ± 1
PEI/8	488 ± 1	697 ± 1	46 ± 1
PEI/10	485 ± 1	680 ± 1	43 ± 1

where P/l is the permeance of the hollow fiber (cm^3 (STP)/cm^2 s cm Hg), Q_i is the volumetric flow rate of gas i at standard temperature and pressure (cm^3 (STP)/s), Δp is the pressure difference between the feed side and the permeation side of the membrane (cm Hg), A is the membrane surface area (cm^2), n is the number of fibers in the module, D is an outer diameter of hollow fiber (cm), and l is an effective length of hollow fiber (cm).

Results and Discussion

Effect of PVP composition on thermal properties of precursor membranes

One of the main criteria that need to be fulfilled by the polymer precursor membranes is high thermal stability (high T_g), by which they can sustain high temperature process. Measurement of thermal properties has widely studied by previous researchers to confirm that the polymer is suitable for carbon membrane preparation.[8,9,14,25,26] In this work, thermal analysis by means of DSC and TGA were used to study the precursor membrane behavior during heat-treatment process and to measure the thermal properties of the PEI, PVP, and polymer blends of PEI/PVP. The weight loss of the membrane samples during heat treatment can be estimated from TGA profile. Generally, lower weight loss will be observed for polymer with high T_g. The decomposition temperature also can be estimated using TGA.

In this work, all the prepared carbon membranes showed a significant shrinkage and turned into black after carbonization process up to 923 K. T_g is one of the temperatures within a glass transition region where the metastable melt transforms into glass in the course of its cooling and where glass transforms into metastable melt in the course of heating. To evaluate the T_g value of the polymers, the heating curves were mostly used by previous researchers. The T_g value for all the samples are summarized in Table 2. The occurrence of single T_g in the polymer blends indicated that both polymers formed a thermodynamically compatible mixture.[7,27] This can be confirmed by visually observing the clear yellow polymer solution formed on mixing two polymers with solvent. The T_g values of PEI/PVP precursor membranes for different PVP compositions were almost similar and slightly lower than pristine PEI. The T_g of the pristine PEI was found at 493 K. After the addition of PVP within the range of 6–10 wt %, the values of T_g were decreased about 3%. In other words, the changes in T_g value for polymer blends of PEI/PVP can be negligible, confirming that T_g for the polymer blends PEI/PVP was not significantly affected by the PVP composition.[28] This might be due to small amount of PVP added in preparing PEI/PVP blends membranes. The T_g of PVP polymer was observed at around 453 K and it is consistent with T_g for its commercial grades.

Figure 1 shows the thermal decomposition behaviors of PEI, PVP, and the polymer blend of PEI/PVP. As illustrated in Figure 1, PEI was stable up to approximately 753 K while PVP started to decompose at temperature of 653 K. The total weight loss of the PVP was estimated to 80% when the temperature reached to 756 K, indicating low thermal stability of this polymer. Meanwhile, for the polymer blends of PEI/PVP, the decomposition occurred at the temperature of 673, 633, and 603 K for PVP composition of 6, 8, and 10 wt %, respectively. It is showed that the thermal stability of the pure PEI was slightly decreased with the addition of thermally labile polymer, PVP. The weight loss of PEI/PVP was more pronounced than pure PEI at higher temperature. It is observed that the total weight loss of the polymer blends increased as the composition of PVP increased. Results show that the total weight loss for PEI/PVP precursor of 6, 8, and 10 wt % PVP were 53%, 54%, and 57%, respectively, of its original weight. Moreover, the total weight loss of PVP having a low thermal stability was 85%, while that of PEI was 50%. It is noteworthy that a large weight loss of 10–50% was observed in a narrow temperature range from 723 to 873 K, which can be attributed to the removal of residual solvent and thermal degradation of functional groups in the membranes by release of small gases (CO and CO_2). However, the weight loss rate was decreased when the temperature reached 903 K due to the rearrangement of carbon structure.[11,12,25] Similar trends and thermal behavior were also found for polymer blends of PPO/PVP[9,26] and PI/PVP.[8,14]

Furthermore, the degradation temperature (T_d), which is defined as the temperature corresponding to 5% weight loss, is always considered as the criterion in determining the thermal stability of high-temperature polymer. The results reveal that the PEI/PVP precursor membranes demonstrated high thermal stability and are suitable for carbon membrane fabrication. As summarized in Table 2, the thermal analysis data obtained from both TGA and DSC were very useful and important to determine the suitable temperature for stabilization and carbonization step during heat-treatment process. The TGA and DSC measurements were performed three times and these data were based on the average value.

During heat-treatment process, stabilization is one of the steps typically involved in the fabrication of carbon membrane and is carried out prior to carbonization step. This step is normally performed in air atmosphere between 423 and 733 K, depending on the type of precursor used. It is believed

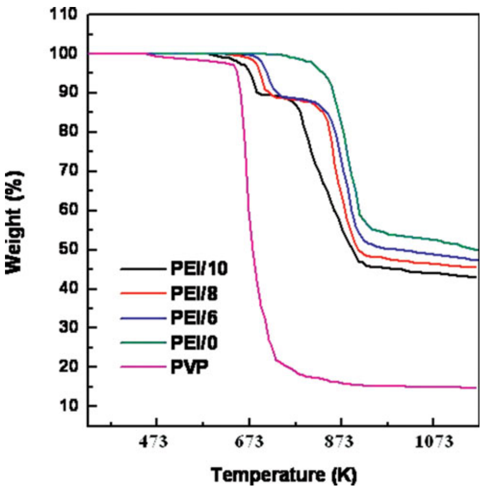


Figure 1. TGA profile for the PVP, PEI, and polymer blends of PEI/PVP.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

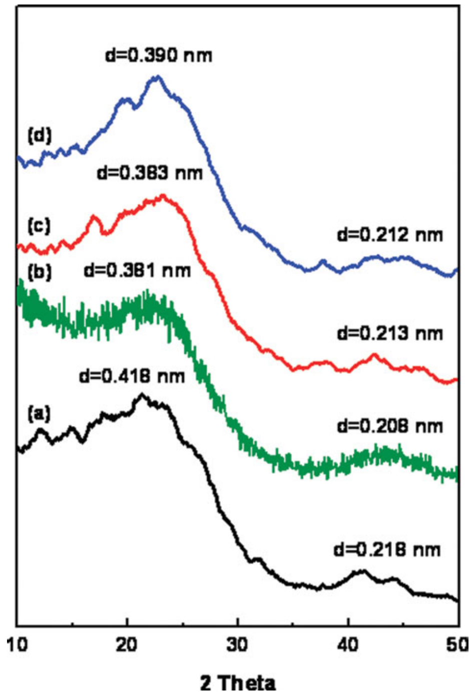


Figure 2. XRD spectra of carbon membrane carbonized at 923 K for different PVP compositions: (a) PEI/0, (b) PEI/6, (c) PEI/8, and (d) PEI/10.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that greater stability membranes are obtained after stabilization under air atmosphere mainly due to the contribution of oxygen in the dehydrogenation reaction. In fact, oxygen mainly acts as a dehydrogenation agent in the conversion of C—C bonds to C=C bonds and generates oxygen-bearing groups in the polymer backbone, such as —OH and C=O. These kinds of groups promote intermolecular crosslinking of the polymer chains and provide greater stability to sustain high temperature in the subsequent carbonization step. Besides that, stabilization also offers the potential to prevent the melting and fusion of the precursor membranes and avoid excessive volatilization of carbon element.[6,29,30]

After stabilization step, the membranes were subjected to carbonization step, during which most chemical reaction and volatile emission occur and part of the heteroatoms originally present in the polymer structure was eliminated while leaving behind a crosslinked and stiff carbon matrix. Typically, carbonization step is carried out at temperatures ranging from 773 to 1273 K, which are between the decomposition temperature and graphitization temperature of the precursor. The pore structure that formed during this step also would determine the separation properties of the resultant carbon hollow fiber membrane.[31]

Effect of PVP composition on microstructure of carbon membrane

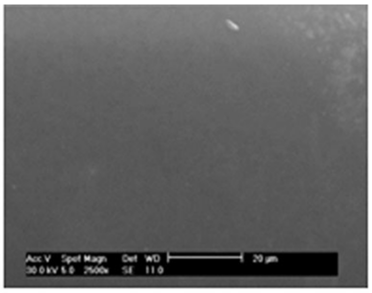
The *d*-spacing value obtained from XRD method is related to the interplanar distance (interchain spacing) in structure of carbon membranes that can be determined from the maximum intensity. Carbon materials with different regular, ordered dimensions and amorphous morphologies should exhibit different XRD spectra profiles. The most relevant peaks when examining polymer-based carbon are the (002) and (100) peaks as stated by Geiszler.[32] The (002) peak is commonly used to determine the crystal length, which can be attributed to the turbostratic structure with randomly oriented graphitic carbon layers,[12] while the (100) peak is related to the distance between carbon atoms on the same plane. Generally, the width of the (002) and (100) peaks is larger in polymer-based carbons than the more defined peaks of well-ordered graphite. XRD patterns of the carbon membranes prepared at 923 K for PEI and polymer blends of different PVP compositions are presented in Figure 2. All the samples expressed a broad peak, indicating that the structure of PEI and polymer blends of PEI/PVP is amorphous.

As presented in Figure 2, the spectrum of the PEI-derived carbon membranes shows a broad reflection at 2θ of 21.25° (0.418 nm). Meanwhile, a slight shift of the peak toward lower angles from 23.35° to 22.80° was observed at higher PVP composition, indicating that the *d*-spacing had become greater, due to the diffraction of (002) plane in graphite. It can be concluded that the *d*-spacing value increased as the PVP composition increased as compared to carbon membrane prepared from pure PEI. The *d*-spacing of the carbon membranes prepared from 6, 8 and 10 wt % of PVP was 0.381, 0.383, and 0.390 nm, respectively. The difference in *d*-spacing among carbon membranes can give useful information on the gas permeance and selectivity of the carbon membranes. This is because the change of the *d*-spacing values depends on the dimensions of the amount of space available for small gas molecules to penetrate through the carbon membranes.[33]

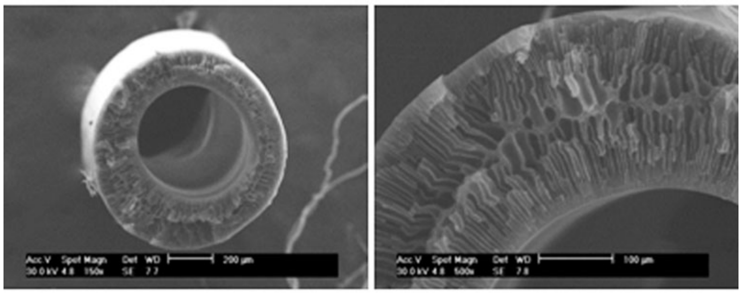
Moreover, another peak due to the (100) diffraction was observed at approximately 41°–43° for all the samples. The results reveal that an ordered carbon structure is formed in the prepared carbon membranes. This result is in agreement with the findings reported for carbon membrane derived from polymer blends of PI/PVP.[8] In the case of polymer blends of poly(phthalazinone ether sulfone ketone) (PPESK), the *d*-spacing values of the resulting carbon membranes were not significantly changed after the addition of PVP.[25]

Effect of PVP composition on morphological structure of carbon membranes

Figures 3–6 show the outer surface and cross-section microphotographs of the carbon membranes prepared from PEI/0, PEI/6, PEI/8, and PEI/10, respectively. It can be observed in Figures 3a and 4a that the carbon membranes derived from PEI/0 and PEI/6 have smooth surface with almost no defect on the outer surface of the fiber. Meanwhile, for carbon membrane derived from PEI/8 (Figure 5a) and PEI/10 (Figure 6a), few open pores and some defects on the outer surface of the fibers can be detected. Figures 3–6 (panel b) represent the cross-section microphotographs of the carbon membranes prepared from different PVP compositions. As can be seen, the carbon membranes prepared from PEI/0 and PEI/6 demonstrated two dense layers, both outer and inner layer with porous sublayer in between. This structure was generated during the dry/wet spinning process as the result of the phase inversion between polymer solution and coagulation liquid. However, the dense structure membrane was observed for carbon membrane prepared from PEI/8 and PEI/10. The differences in the structure of these resultant carbon membranes can probably be attributed to the composition of the PVP used in its precursor membrane. The same structure properties were also observed for carbon membrane derived from polymer blending between PAN and PVP prepared by Linkov et al.[7]



(a) Outer surface



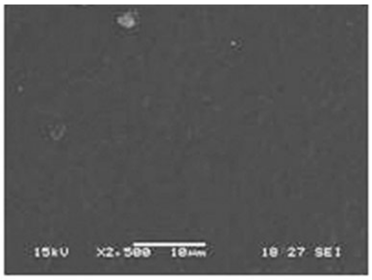
(b) Cross section

Figure 3. SEM microphotographs of (a) outer surface and (b) cross-section of the carbon membrane prepared from PEI/0.

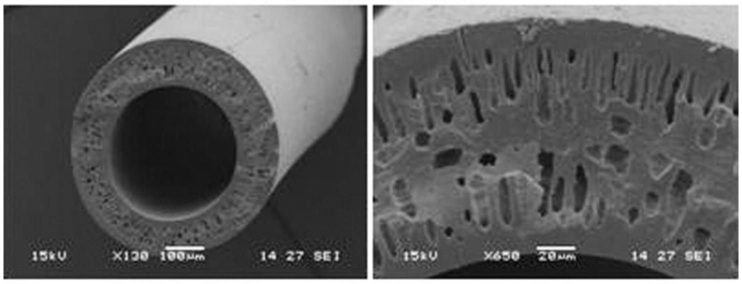
In addition, there is no cross-section deformation, and irregularities were observed for all the fibers. It shows that the precursor was fully stabilized at 300°C under air flow. The similar finding has been reported by Coutinho et al.[11] and Linkov et al.[7] The diameter of the resultant carbon membranes was also significantly affected by the composition of the polymer used during precursor membrane preparation. The diameter of the carbon membranes prepared from low PVP composition (PEI/0 and PEI/6) was greater than those prepared from high PVP composition (PEI/8 and PEI/10). It indicates that the physical shrinking of the membrane due to the precursor decomposition and the evolution of the compounds during the heat-treatment process were more pronounced in carbon membrane derived from high PVP composition. This is because PVP polymer was easy to decompose at high process temperature. This is corresponding to the weight loss observed for the membrane under TGA test. Overall, the microphotograph reported in this work is in agreement with PEI-based supported carbon membrane previously studied by Rao et al.[12] and Sedigh et al.[31]

Effect of PVP composition on gas permeation properties of carbon membranes

Carbon membrane derived from polymer blends of PEI/PVP with different PVP compositions was prepared to investigate the effect of the addition of thermally labile PVP in precursor membranes on gas permeation properties of the

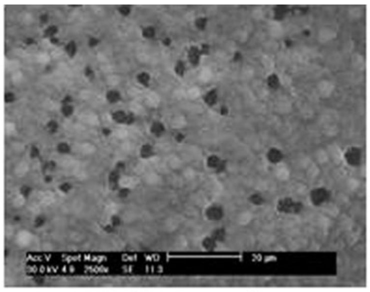


(a) Outer surface

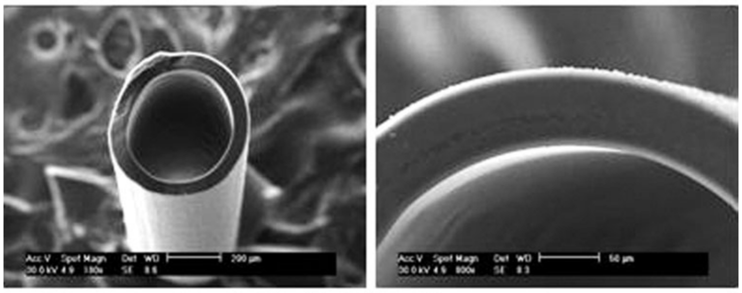


(b) Cross section

Figure 4. SEM microphotographs of (a) outer surface and (b) cross-section of the carbon membrane prepared from PEI/6.



(a) Outer surface

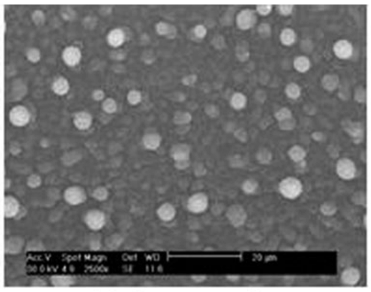


(b) Cross section

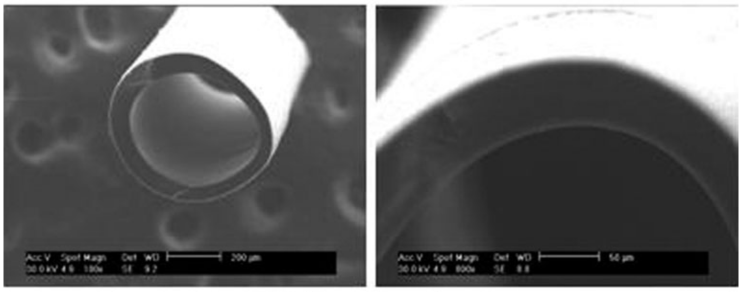
Figure 5. SEM microphotographs of (a) outer surface and (b) cross-section of the carbon membrane prepared from PEI/8.

resultant carbon membranes. Gas permeation properties of PEI- and PEI/PVP-derived carbon membranes were measured via single gas permeation apparatus. Figure 7 represents the gas permeance of gas species for the prepared carbon membranes at different PVP compositions. All the carbon membranes were stabilized at 573 K under air atmosphere followed by carbonization up to 923 K under N_2 atmosphere.

As illustrated in Figure 7a–c, the gas permeance of PEI-derived carbon membranes was higher than those of PEI/PVP-derived carbon membranes. It is because the preparation of PEI-derived carbon membrane with defect-free surface areas with sufficient mechanical strength for gas separation measurement was more difficult compared to those PEI/PVP derived carbon membrane. This might be due to the low total polymer concentration used which leads to low viscosity of the polymer solution. As a result, a more permeable membrane was obtained for PEI-derived carbon membranes. In contrast, the viscosity of the polymer blends was increased with the addition of PVP that makes it easier to be fabricated as carbon membranes and fewer cracks was created during heat treatment. It can be observed that the gas permeance for all the gases of the prepared carbon membranes increased when the composition of PVP used in precursor membranes was increased from 6 to 8 wt %. The



(a) Outer surface



(b) Cross section

Figure 6. SEM microphotographs of (a) outer surface and (b) cross-section of the carbon membrane prepared from PEI/10.

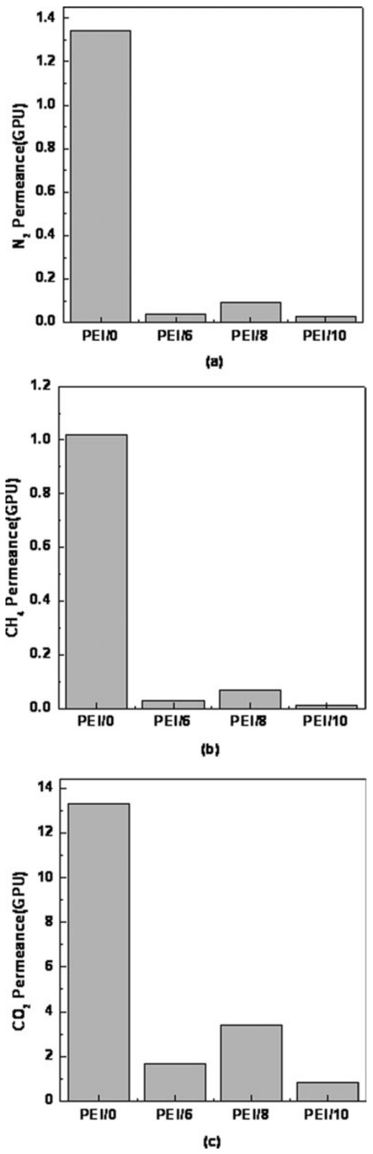


Figure 7. Effects of PVP composition (wt %) on (a) N_2, (b) CH_4, and (c) CO_2 permeance of PEI/PVP-based carbon membranes.

increases of more than 50% were observed for the permeance of N_2, CH_4, and CO_2, respectively. It is mainly due to the enhancement of diffusional pathways of the gas molecules transport through carbon membranes, enabling small gas molecules to pass through the tiny channels in the carbon membranes. As PVP can be easily decomposed at a lower temperature compared to PEI, the preparation of the carbon membranes from polymer blends PEI/PVP, thus, can lead to the formation of porous structure. In general, the decomposition of the PEI would form micropores (<2 nm), while PVP decomposition might lead to the formation of mesopores (2–50 nm) during heat-treatment process.[8,14,34] These micropores are created because of small gaseous molecules channeling their way out of the solid matrix during heat-treatment process and would further closed by high temperature process.[29] Similar behavior was also observed in Refs. [7] and [9] where carbon membranes derived from polymer blends containing PVP demonstrated high porosity structure and narrow pore size distribution.

In contrast, the permeation results for the carbon membrane decreased when 10 wt % PVP was added and it is mainly due to the extremely high viscosity of the polymer blend solutions that tends to produce dense structure membranes. It is believed that the structure of the resulting carbon membranes strongly depends on the structure of their precursor membranes.[7] Thus, dense carbon membranes would be produced in this case. Based on gas permeation data, the gas permeance of the tested gases were in the order $CO_2 > N_2 > CH_4$, which consistent with the order of the kinetic diameters of the gas molecules (CO_2 (3.3 Å) > N_2 (3.64 Å) > CH_4 (3.8 Å)). Moreover, the *d*-spacing of the carbon membrane obtained were in the range of 0.38–0.42 nm, which is similar to the kinetic diameters of the tested gases. This indicates that the gas permeation through these carbon membranes obeys molecular sieving mechanism. This result is in agreement with the work reported by previous researchers.[12,30]

The selectivities of CO_2/CH_4 and CO_2/N_2 in the resulting carbon membranes as a function of PVP composition are shown in Figure 8. Compared to those prepared from PEI-derived carbon membranes, the selectivity of both gas pairs remarkably increased with the addition of 6 wt % of PVP and slightly decreased when PVP composition of 8 wt % was used. As can be seen in Figure 8, the selectivities of CO_2/CH_4 and CO_2/N_2 for carbon membranes derived from pure PEI were 13.06 and 9.94, respectively. The values, however, increased up to 55.33 and 41.50 on addition of 6

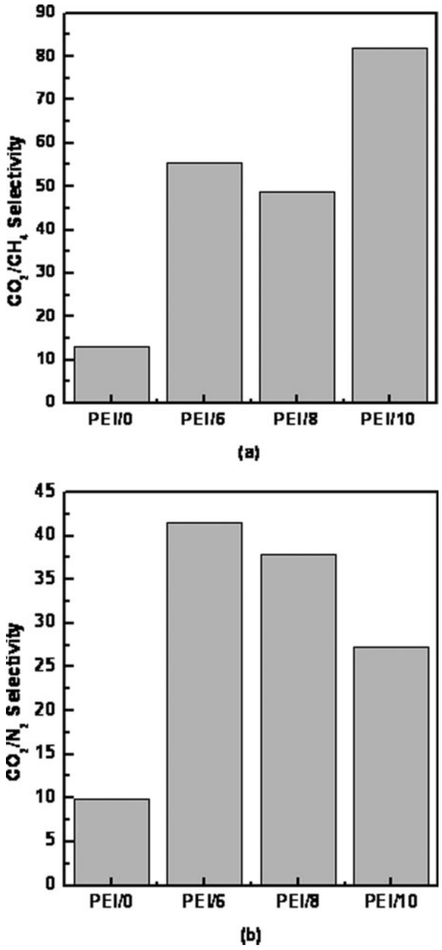


Figure 8. Effects of PVP composition (wt %) on (a) CO_2/CH_4 and (b) CO_2/N_2 selectivities of PEI/PVP-based carbon membranes.

wt % PVP, indicating decrease in pore dimension of the resulting carbon membranes by the addition of PVP.[34,35] The selectivities of both CO_2/CH_4 and CO_2/N_2 obtained were also much higher than those from Knudsen diffusion, which confirmed that the pores of the prepared carbon membrane are of molecular dimensions.

Previous experimental results reported the configuration types and membrane performance for carbon membranes published recently encompassing a variety of precursor blends summarized in Table 3. It is important to note that the present PEI/PVP-based carbon hollow fiber membranes showed superior performance compared to other reported in the literature.[36,37] Variations in CO_2/CH_4 and CO_2/N_2 selectivity values through carbon membranes can be found also with membranes fabricated from similar precursors and at equivalent heat-treatment protocol. This is manifested as variations in gas selectivity with membrane preparation methodology and configuration type. Compared to the PEI/PVP-based carbon membranes produced by Rao et al.,[12] remarkable enhancements in CO_2/N_2 selectivity of about three times were observed. In the case of CO_2/CH_4 selectivity, carbon membranes derived in this study showed higher value compared to previous research using PPO/PVP, P84 copolyimide and Matrimid as a precursor. Based on this study, carbon membrane of hollow fiber configuration with CO_2/CH_4 and CO_2/N_2 selectivities of 55.33 and 41.50, respectively, were obtained. This result is very good relative to current attractive polymeric membranes, which have CO_2/CH_4 and CO_2/N_2 selectivities typically ranging from 30 to 50 and 25 to 45, respectively.[21,38]

Furthermore, most of the gas permeation data reported by previous researchers were using permeability (Barrer) in their article, since most of them were prepared in the supported form (flat sheet and tubular). The experimental data obtained in the literature using permeance (GPU) in the gas permeation study are listed in Table 4 for comparison purposes. As can be seen in Table 4, compared to the P84 copolyimide-based carbon membranes produced by Favvas et al.[36] an improvement in N_2, CH_4, CO_2 permeance value is observed. Carbon membranes derived from Matrimid shows more permeable behavior for all gases but less selective than P84 copolyimide and PEI/PVP-derived carbon hollow fiber membranes. According to gas permeation data acquired from this work, it is proved that carbon membrane derived from PEI/PVP has a potential to compete with available polymeric membranes in the market. This might be due to the adaptation of hollow fiber configuration in preparing carbon membranes.

In practice, carbon membranes have been fabricated in two main configurations which are unsupported membranes (flat membranes, capillary tubes, or hollow fibers) and supported membranes (flat or tubular) on a macroporous material.[6,11] The use of hollow fiber geometry has long been a solution to improve the performance of membrane-based separation processes especially in gas separation. The main beneficial features contributed by hollow fiber are high separation efficiency, high active surface area to volume ratios (>1000 m^2/m^3), able to operate at high pressure drops, and low production cost as compared to other types of configuration.[39,40] Although supported carbon membrane is the most popular due to its simple preparation, this type of configuration, however, exhibits a problem in depositing polymer solution on the support uniformly. The cycle of polymer deposition–heat treatment needs to be repeated several times to obtain an almost defect-free membrane. There are several methods to deposit the polymer solution on the support such as dip coating, spin coating, spray coating, and ultrasonic deposition.[4–6] This can be concluded that the gas permeation performance of the resulting carbon membranes was also affected by the types of their configurations.

Table 3. Permeation Performance of the Derived Carbon Membrane Prepared by Previous Researchers

		Selectivity	
Heating Rate	Configuration	CO_2/CH_4	CO_2/N_2
P84 copolyimide[36]	Hollow fiber	38.9	42.8
Matrimid[37]	Hollow fiber	20.86	23.6
PEI/PVP[12]	Flat sheet		13.70
PI/PVP[8]	Flat sheet		~40.00
PI/PVP[14]	Flat sheet		30.00–38.00
PPO/PVP[9]	Tubular	~10.00	~20.00
PPESK/PVP[25]	Flat sheet		25.70
PEI/PVP*	Hollow fiber	55.33	41.50

*This work.

Table 4. Carbon Hollow Fiber Membranes Prepared by Previous Researchers

	Permeance (GPU)			Selectivity	
Precursor	N_2	CO_2	CH_4	CO_2/CH_4	CO_2/N_2
Matrimid[37]	0.270	6.300	0.300	20.86	23.60
P84 copolyimide[36]	0.006	0.276	0.007	38.90	42.80
PEI/PVP*	0.04	1.66	0.03	55.33	41.50

*This work.

Conclusions

This research is part of an effort to convince that carbon membrane is one of the materials that need to be considered for gas separation applications in the future. Carbon hollow fiber membranes fabricated from polymer blends PEI/PVP were successfully prepared. Based on the results obtained from this study, several conclusions can be derived:

1. TGA analyses of the PEI/PVP precursor membrane showed a shift of the weight loss curves toward lower temperatures with respect to pure PEI membranes. The presence of PVP caused slight decrease in thermal stability properties of the polymer blends PEI/PVP.
2. Overall, the polymer blends with 6 wt % PVP seems to be the best composition in the preparation of PEI/PVP-based carbon hollow fiber membranes with CO_2/CH_4 and CO_2/N_2 selectivities of 55.33 and 41.50, respectively.
3. Although PEI and PVP blending could enhance the CO_2/CH_4 and CO_2/N_2 selectivity of the resulting carbon membranes, the permeance of the examined gases (N_2, CH_4, and CO_2) was affected.
4. Compared to literature data of gas separation performance for carbon membrane derived from different polymer blends precursor, PEI/PVP-derived carbon hollow fiber membranes exhibited superior performance.

The promising performance obtained from this study makes worth for any further research in gas separation applications using polymer blends derived from carbon hollow fiber membranes.

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Notation

PEI = polyetherimide
PVP = polyvinylpyrrolidone
PPO = polyphenylene oxide
PAN = polyacrylonitrile
PEG = polyethylene glycol
PI = polyimide
PPESK = poly(phthalazinone ether sulfone ketone)
T_g = glass transition temperature
T_d = degradation temperature
N_2 = nitrogen
CO_2 = carbon dioxide
CH_4 = methane

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