

Effect of Stabilization Temperature on Gas Permeation Properties of Carbon Hollow Fiber Membrane

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ABSTRACT: Carbon hollow fiber membranes (CHFMs) derived from polymer blend of polyetherimide (PEI) and polyvinylpyrrolidone (PVP) were extensively prepared through stabilization under air atmosphere followed by carbonization under N₂ atmosphere. The effects of the stabilization temperature on the morphological structure, chemical structure, and gas permeation properties were investigated thoroughly by means of scanning electron microscopy, Fourier transform infrared spectroscopy, and single gas permeation system. The experiment results indicate that the transport mechanism of small gas molecules of N₂, CO₂, and CH₄ is dominated by the molecular sieving effect. Based on morphological structure and gas permeation properties, an optimum stabilization condition for the preparation of CHFMs derived from PEI/PVP was found at 300°C under air atmosphere. The selectivity of 55 and 41 for CO₂/CH₄ and CO₂/N₂, respectively, were obtained for CHFMs prepared at stabilization temperature of 300°C. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

There are several points within stationary energy production where CO₂ is produced and then emitted to the atmosphere, such as in the production of natural gas from an underground reservoir and in the production of synthesis gas using fossil fuels and flue gas from electricity power stations that are from direct combustion of fossil fuels.^{1,2} Usually, CO₂ is the most abundant contaminant in a typical natural gas feed, with some large reservoirs containing over 50% CO₂. In this case, it is mandatory to remove the CO₂ from other gas mixtures to meet the environment regulations as well as to meet the pipeline specifications. Currently, capture of CO₂ with amine solvents is the most mature technology and the other technology includes various solid adsorbent systems and cryogenics. Such systems, even though widely used, can pose operational difficulties due to the problems involved in keeping the solvent clean and operating within the process constraints of the system.³

Owing to the relatively low energy requirements (no phase changes), smaller footprint, reduced environmental impact (no toxic solvents), easier operation (no moving parts or liquid flow problems), no corrosion issues and inherent modularity (constant contact area), polymer-based carbon membrane has been

considered to be a promising technique for CO₂ capture.^{4–8} According to Baker,⁹ one of the current membrane markets is dominated by natural gas purification. Therefore, the gas permeation properties of the carbon membrane prepared in this article were concentrated on the CO₂ separation. Carbon membrane is one of the new emerging materials that have been extensively studied for gas separation application. It is found that carbon membranes can be prepared from a wide range of polymeric precursors such as polyimides (PI), polyetherimide (PEI), phenolic resin, polyfurfuryl alcohol, polyphenylene oxide (PPO), poly(vinylidene chloride-co-vinyl chloride), polyacrylonitrile (PAN), and phenol formaldehyde resin (PFR).^{10–12} Although significant research works have been made since carbon membranes inception, there remains the need to significantly improve the permeation properties of these membranes if they are to become viable for real applications.

Most of the polymer precursors used to fabricate carbon membranes are commercially expensive materials and even some of them are exclusively obtained at laboratory scale. Therefore, the works develop in this study focus on the use of inexpensive and commercially available polymers as precursors of carbon membranes. PEI was chosen as the main polymer for being

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inexpensive compared with other polyimide additives, availability, and polyimide-like structure. PEI is an attractive polymeric membrane material because of its excellent thermal, chemical, and mechanical stabilities. The glass transition temperature of this material is 216°C.¹⁰ The early study on the preparation of carbon membranes from PEI was conducted by Fuertes and Centeno on 1998.¹³ A year later, Sedigh et al.^{14,15} had prepared PEI-coated mesoporous tubular support for CO₂/CH₄ and H₂/CH₄ separation. After that, there was not much research involving the use of PEI as a precursor for carbon membranes applied in gas separation until in 2008, when Rao et al.¹⁶ prepared their supported carbon membrane from PEI precursor. Even the studies on the structural morphology of PEI-based carbon hollow fiber membrane (CHFMs) have reported by Coutinho et al.,¹⁷ but there is no available data on the gas permeation properties has been published. Moreover, most of the research on carbon membrane for gas separation has been prepared in supported membranes. There are few scientific paper works dealing with the gas permeation properties through hollow fiber membranes at high feed pressures. Thus, the fabrication of PEI/polyvinylpyrrolidone (PVP)-based carbon membranes using hollow fiber geometry is conducted.

Recently, the development of carbon membrane separation using polymer blends material as a starting material has become popular and significant. This is because the heat treatment of blended polymers led to the creation of two different porous carbon structure; mesoporous and microporous which could affect the gas permeation properties. It is found that a good combination of permeability and selectivity could be achieved by the introduction of polymer with different thermal properties with main polymer in dope solution.¹⁸ An early work regarding the use of polymer blend as a carbon material precursor was disclosed by Ozaki et al. in 1997.¹⁹ In recent years, several carbon membranes fabricated from other polymer blends have also been reported. Those include blending of PPO/PVP,²⁰ PEI/PVP,^{16,17} PAN/polyethylene glycol (PEG),²¹ PAN/PVP,²¹ PI/PEG,¹⁸ PI/PVP,^{22,23} PFR/PEG,²⁴ and polybenzimidazole (PBI)/PI.²⁵ In this study, PVP was used as a second polymer to produce PEI/PVP polymer blends precursor. The combination of PEI/PVP was also reported to be a great potential due to their easy preparation technique.²¹

Besides, attempt through the appropriate heat treatment conditions has also been employed since different polymeric precursor membranes will produce different structure of the final carbon membranes. Many researchers have reported that the microstructure of carbon membranes (pore size, pore volume, and pore distribution) could be tailored by controlling the conditions of heat treatment process.^{2,17,20,26-34} By preparing CHFMs under different heat treatment conditions, valuable information on the structural evolution and gas permeation properties of PEI/PVP-based CHFMs is obtained.

Stabilization or pre-oxidation process is one of the steps involved in the fabrication of carbon membrane and is carried out before the carbonization process. Most of the prepared high performance carbon membranes have been successfully stabilized in air atmosphere between 150 and 460°C, depending on the type of polymer precursor used. It is believed 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 back-bone, 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 process. If the stabilization process is not completed throughout the entire membrane cross section, a significant weight loss can occur at higher temperature.^{17,30,10}

Basically, the stabilization process performed in carbon membrane preparation is also similar to the stabilization process carried out in carbon fiber preparation. During the stabilization process, the precursor would undergo a number of physical and chemical changes due to a variety of exothermic chemical reaction, including decomposition, dehydrogenation, oxidation, and crosslinking.^{35,36} In this study, carbon membrane derived from polymer blend of PEI/PVP in self-supporting form for CO₂ separation were prepared. The PEI polymer is a kind of thermoplastic polymer, which would go through a melting or softening stage during carbonization step. However, the melting stage is unfavorable for the preparation of the carbon membranes. It is because the microporous structure evolved would be destroying due to the removal of functional groups in the form of volatiles or gases during carbonization. As a result, stabilization step prior to carbonization is recommended to prevent thermoplastic polymers from melting stage at high temperatures and helps to maintain the morphology and structure of the precursor in the resultant carbon membranes.^{37,38}

Studies have found that stabilization between the glass transition temperature (T_g) and degradation temperature (T_d) can effectively prevent a melting stage during carbonization for thermal plastic polymers, such as PEI,¹⁷ polyimide,^{39,40} phenolic resin,²⁸ and PAN.⁴¹ Further details of the stabilization conditions that have been applied by previous researchers can be found in the literature.¹² To date, the literature on the derived CHFMs from PEI/PVP for gas separation is very limited, especially with regards to the effect of the stabilization conditions on the properties of the resultant carbon membrane. Also, the stabilization study and its effects on the subsequent carbonization process remains an area requiring further clarification. Thus, the design of PEI/PVP-based CHFMs is engineered to study the properties of the resultant carbon membranes as well as their permeance and selectivity by manipulating the stabilization temperatures. In pursuit of this goal, the membranes were extensively characterized by means of scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and single gas permeation measurement.

EXPERIMENTAL

CHFMs 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 120°C prior use. The chemical *N*-methyl-2-pyrrolidone (NMP) with analytical grade was used as solvent without any purification. Polymeric hollow fiber membranes with 17 wt % PEI/6 wt %

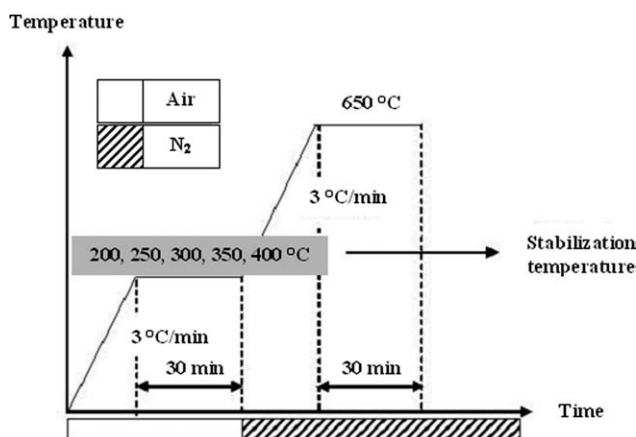


Figure 1. Heat treatment profile.

PVP was used as a precursor membranes. These membranes were fabricated using dry/wet spinning process. The details on the experimental procedures included spinning condition used in this study can be found elsewhere.⁴² 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. Precursor membranes were subjected to stabilization step under five different temperatures before undergoes carbonization step at high temperature. In the first step, the precursor membranes were stabilized under compressed air atmosphere (200 mL/min) at various temperatures (200, 250, 300, 350, and 400 °C) with a heating rate of 3 °C/min. At this stage, the membranes were held for 30 min. Subsequently, the temperature was increased to final carbonization temperature of 650 °C with the heating rate of 3 °C/min and holding it constant for 30 min under N₂ flow (200 mL/min). At last, the membranes were cooled down naturally to room temperature. The detailed of the heat treatment profile is illustrated in Figure 1. The nomenclature of resultant CHFMs is given in the form of CM – stabilization temperature.

CHFMs Characterization

Morphological structure images were obtained in a JEOL JSM-5610LV SEM. FTIR analysis was taken in a Nicolet (Magna-IR 560) spectrometer to display the change of the functional groups and elemental in the membranes when they were heated from room temperature to carbonization temperature.

CHFMs Performance Measurement

The membrane performances were measured by two important parameters: permeance and selectivity. These parameters were examined using a single gas permeation system. Prior to analysis, the membrane samples were assembled in the module. The effective length of each hollow fiber was 10 cm, which corresponds to a total permeation area of 21 cm² in the membrane module. 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.³¹ The following gases were chosen as those with the potential for separation; CO₂, N₂, and CH₄. The permeance was determined in the sequence of N₂, CH₄, and CO₂ at room temperature and 7 Bar. Each measurement value is the result of three different mem-

branes 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):

$$\left(\frac{P}{l}\right)_i \frac{Q_i}{\Delta p \cdot A} = \frac{Q}{n\pi D l \Delta P} \quad (1)$$

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

Selectivity, α :

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \quad (2)$$

where P/l is the permeance of the hollow fiber [cm³ (STP)/cm² s cmHg], Q_i is the volumetric flow rate of gas i at standard temperature and pressure [cm³ (STP)/s], Δp is the pressure difference between the feed side and the permeation side of the membrane (cmHg), A is the membrane surface area (cm²), 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

Figure 2 depicts the morphological structure of the resultant CHFMs prepared under different stabilization temperatures together with the CHFMs prepared from pristine PEI. It can be seen that the two dense layers, both outer and inner layer with porous sublayer in between was obtained for all the resultant CHFMs. In overall, the similar membrane structure was obtained for both CHFMs derived from PEI and PEI/PVP. This structure was generated during the dry/wet spinning process as the result of the phase inversion between polymer solution and coagulation liquid. This reveals that the structure of the membranes is preserved after heat treatment process and any arrangement of the structure on precursor membrane does not occur during stabilization and carbonization steps.

Moreover, there are cross section deformations and irregularities were observed for all the resultant PEI/PVP-based CHFMs except for PEI/PVP-based CHFMs prepared under stabilization temperature of 300 °C and PEI-based CHFMs. It is shows that the precursor was fully stabilized and the oxidation reactions were more effective at 300 °C under air flow. The similar finding has been reported by Linkov et al.,²¹ Sedigh et al.,¹⁴ Coutinho et al.,¹⁷ Rao et al.,¹⁶ and Xu et al.⁴³

Additionally, the dissolution tests were also carried out to determine the crosslinking degree of a polymeric precursor membrane obtained during stabilization step. It is suggested that the optimum stabilized membranes have much higher organic solvent stability than the incomplete stabilized membranes.^{44,45} For PEI/PVP, the polymeric precursor membranes used here were totally soluble in NMP. When treated in air at 200 and 250 °C, the stabilized membranes dissolve partially in NMP and some swollen pieces appeared. This suggests that some crosslinks have

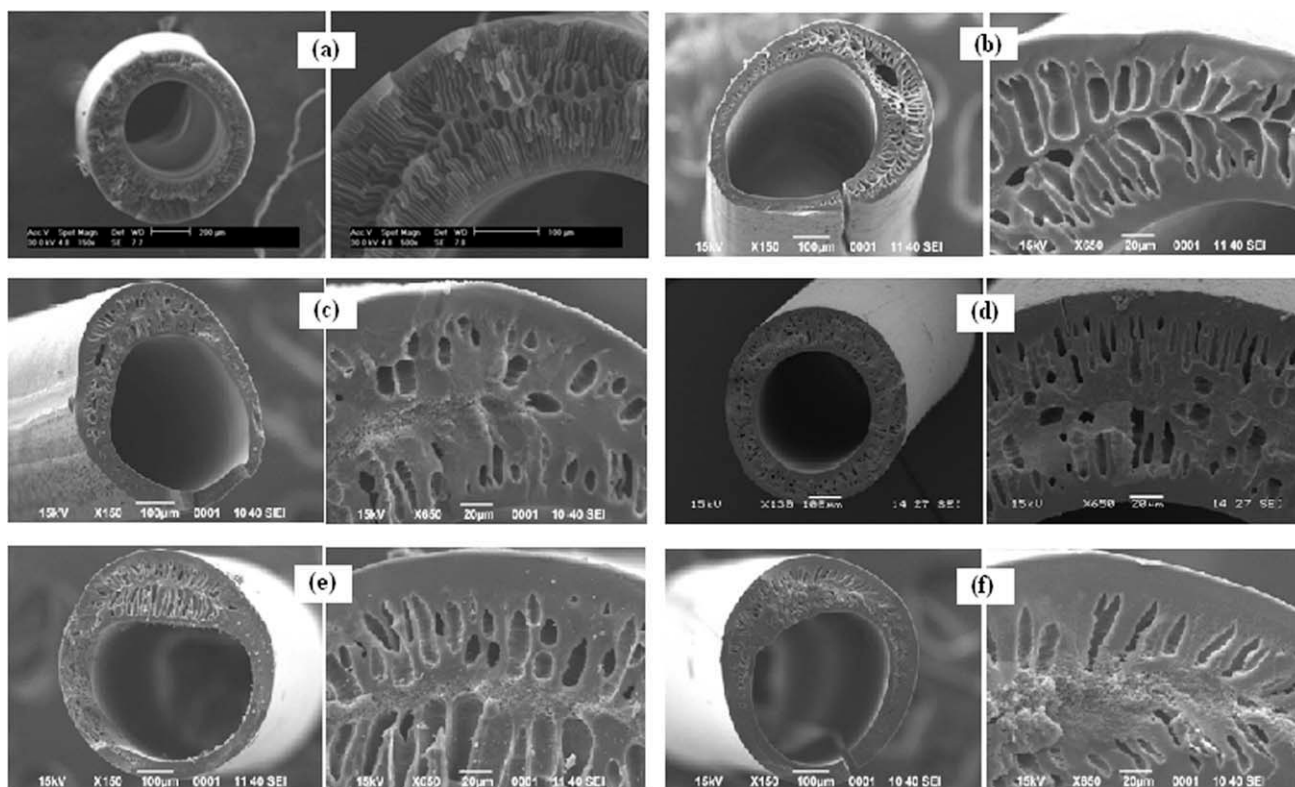


Figure 2. SEM microphotographs of the (a) PEI-based CHFMs and PEI/PVP-based CHFMs prepared under different stabilization temperatures; (b) 200°C, (c) 250°C, (d) 300°C, (e) 350°C, and (f) 400°C.

begun to form, but crosslinking has not proceeded sufficiently to stabilize the membranes in overall. After treating in air above 300°C, the infinite molecular weight makes the membranes insoluble in NMP, indicating that stabilization caused by oxidation and cross linking reaction in the polymer structure has proceeded sufficiently to stabilize the CHFMs.

Besides, in terms of mechanical strength, the resultant CHFMs prepared at the stabilization temperature of beyond 300°C exhibited low mechanical strength owing to excessive oxidation during stabilization step. Excess stabilization reduces the alignment of mesogen molecules by enlarging the molecular size. At higher stabilization temperature of 350 and 400°C, excess oxygen presence in the air activates O atoms in the structure to go out as CO or CO₂ to leave defects. Therefore, from the structure and thermostability point of view, it is preferred to stabilize the PEI/PVP-based precursor membranes under air atmosphere around 300°C prior to carbonization step at high temperature.

If the extent of stabilization is high enough, oxygen will attack the membrane and there will be an accompanying with evolution of CO₂. The crosslinking reaction occurred at sufficient stabilization conditions might also reduce the fusion of nodules, and as a result the asymmetric structure of the precursor membranes was well held as shown in SEM microphotograph. In contrast, if the stabilization process is not completed throughout the entire membrane cross section, a significant deformation of the hollow fiber shape and high weight loss would occur at higher temperature process.¹⁷ Moreover, as the stabilization

temperature increased, the degree of decomposition and cross linking in the membrane increased, which resulted in different micropore structures of the CHFMs.

Figure 3 shows the FTIR spectra of the CHFMs prepared under different stabilization temperatures. All the samples showed similar absorption band characteristic and exhibited quite different intensity except for CHFMs prepared under stabilization of 350 and 400°C. The absorption band assigned for C=O and Ar—O—Ar (aryl ether bonds) stretching were appeared at 1510 and 1162 cm⁻¹, respectively, for CHFMs prepared under stabilization of 350°C. Meanwhile, for CHFMs prepared under stabilization of 200, 250, 300, and 400°C, these chemical structure were appeared in the region from 1520 to 1558 cm⁻¹ and 1047 to 1069 cm⁻¹, respectively. All the absorption bands observed were broad and weak, which expected to be disappeared with increasing process temperature. This is because the membrane has decomposed and almost all the chemical structures in the polymeric precursor membranes have converted into carbon structure. The results in agreements to the work reported by Rao et al.¹⁶ and Zhang et al.⁸

Gas permeation properties of the CHFMs derived from PEI and PEI/PVP were measured via single gas permeation system. The influence of stabilization temperature on the gas permeation properties of the resultant CHFMs is summarized in Table I. The result was compared with the CHFMs obtained from pristine PEI. As indicated in Table I, the gas permeance of PEI-derived CHFMs were higher than those of PEI/PVP-derived CHFMs. It

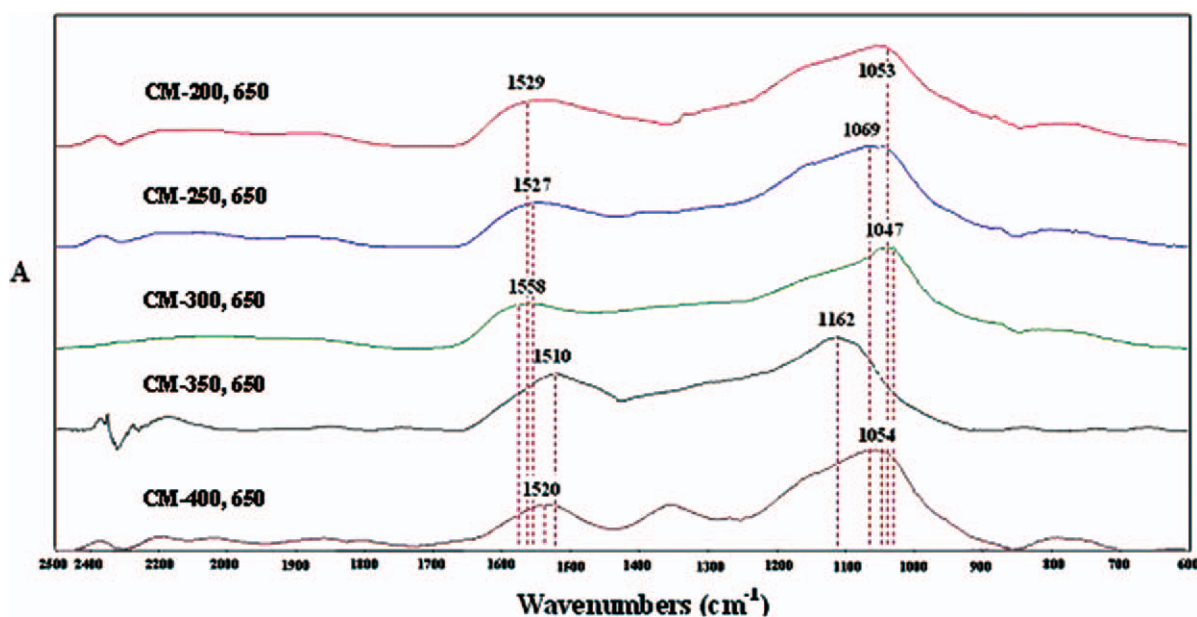


Figure 3. FTIR spectra of the CHFMs prepared under different stabilization temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

is because the preparation of PEI-derived CHFMs with defect-free surface areas and sufficient mechanical strength for gas separation measurement was more difficult compared with those PEI/PVP-derived CHFMs. 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 CHFMs. In contrast, the viscosity of the polymer blends were increased with the addition of PVP that makes it easier to be fabricated as CHFMs and fewer cracks were created during heat treatment. It can be observed that the gas permeance for all the gases of the prepared PEI/PVP-based CHFMs decreased when PVP was added and the values kept decreased as the stabilization temperature increased. This is because the formation of pore structure might be too small for gas molecules to pass through the tiny channels in the structure of the PEI/PVP-based CHFMs. Moreover, the addition of 6 wt % of PVP into the polymer blend PEI/PVP probably too small for the effect of enhancement of diffusional pathways of the gas molecules transport through CHFMs, which could enabled to increase the gas permeance value of the membranes.

As indicated in the Table I, as the stabilization temperature increased from 200 to 350°C, the gas permeance of the CHFMs remarkably decreased. It is due to the deterioration in original backbone of the polymer and formed much more activated points composed of oxygen-containing groups as the stabilization temperature increased, which will affect the developed pore system in the resultant CHFMs. During subsequent carbonization process, the pore structure of the resultant CHFMs shrinks and even collapse to form an impermeable bulk carbon structure by the rapid evolution of those activated points. However, an excessive stabilization reaction may occur at high stabilization temperature, which could lead to the development of defects and an enlargement of the pore size. This is indicated

when the gas permeance of the CHFMs treated up to 400°C under air flow was increased.⁴⁶ The pore size of the resultant CHFMs probably was too large for an effective separation. Also, much more defects were created on the membrane that enabled the gas molecules to pass through the defects easily. It is established that small changes in the pore size of the carbon structure can have a considerable impact on gas permeation properties of the resultant CHFMs because the pore network created in this membrane are similar in size to the gas penetrant.⁴⁷

Based on gas permeation data, the gas permeance of the tested gases were in the order $\text{CO}_2 > \text{N}_2 > \text{CH}_4$, which consistent with the order of the kinetic diameters of the gas molecules [CO_2 (3.3Å) > N_2 (3.64Å) > CH_4 (3.8Å)]. This indicates that the gas permeation through these carbon membranes obeys molecular sieving mechanism. This result is in agreements with the work reported by previous researchers.^{6,16,48} The selectivity of CO_2/CH_4 and CO_2/N_2 as high as 55.33 and 41.50 have been achieved for CHFMs prepared at stabilization temperature of

Table I. Gas Separation Properties of the Resultant CHFMs Prepared at Different Stabilization Temperatures (Error Analysis is about $\pm 10\%$)

Stabilization temperature (°C)	Permeance			Selectivity	
	N_2	CH_4	CO_2	CO_2/CH_4	CO_2/N_2
PEI-based chfm	1.34	1.02	13.32	13.06	9.94
200	0.21	0.20	2.20	11.50	10.48
250	0.08	0.05	1.70	34.00	21.25
300	0.04	0.03	1.66	55.33	41.50
350	0.04	0.02	1.03	51.50	25.75
400	0.15	0.12	1.85	15.42	12.33

300°C. The CHFMs prepared at stabilization temperature of 350°C also exhibited a promising gas separation performance for CO₂/CH₄ and CO₂/N₂ but exhibited the lowest gas permeance for all the tested gases compared with those CHFMs prepared at stabilization temperature of 200, 250, 300, and 400°C.

Beside gas permeation properties, the mechanical stability of the membranes also is one of the issues that need to be considered in producing good performance CHFMs for gas separation application. Although there is no scientific measurement were performed in this research, but the mechanical stability of the membrane was observed during the module construction stage. The CHFMs prepared at higher stabilization temperature of 350 and 400°C was found to be very difficult to handle and an extra precaution was needed as compared with those prepared at low stabilization temperature of 200 to 300°C. The findings are in agreements with Refs. 29, 46, 46, and 50.

Such selectivity that obtained was still in the range of current attractive result for CO₂/CH₄ and CO₂/N₂ separation. This was probably owing to the formation of micropores, which connecting to each others, and mesopores, which do not penetrate through the total thickness of the CHFMs, as demonstrated in the preparation of carbon membrane derived from BPDA-pp'ODA polyimide.⁵¹ Therefore, by considering the morphological structure, dissolution test, mechanical stability, and gas separation performance, the stabilization temperature at 300°C under air atmosphere is the best conditions for PEI/PVP-based CHFMs preparation.

CONCLUSIONS

This study represents the CHFMs derived from PEI/PVP prepared at different stabilization conditions. SEM microphotographs reveal that the structure of the CHFMs is preserved after heat treatment process and any arrangement of the structure on precursor membrane does not occur during stabilization and carbonization steps. It is showed that there is no cross section deformation and irregularities were observed for the CHFMs prepared under stabilization temperature of 300°C. All the absorption bands observed were broad and weak and the intensity of the peak decreased as the process temperature increased. This is because the membrane has decomposed and almost all the chemical structures in the polymeric precursor membranes have converted into carbon structure. This study elucidate that the gas permeance of the CHFMs remarkably decreased as the stabilization temperature increased from 200 to 350°C. As the stabilization temperature increased, the degree of decomposition and cross linking in the membrane increased, which resulted in different gas separation properties of the derived CHFMs. In terms of physical and chemical properties, mechanical strength, and gas permeation performance, the stabilization step at 300°C under air atmosphere show the best condition in the preparation of the PEI/PVP-based CHFMs for gas separation.

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