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Novel approaches to fabricate carbon molecular sieve membranes based on chemical modified and solvent treated polyimides

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Abstract

Two brand-new modification technologies were developed for pyrolyzing the carbon molecular sieve membranes (CMSMs) with excellent separation efficiency. The modifications were performed on polymeric precursors. It is believed that the space filling effect by these modifications could considerably alter the separation performance of resultant carbon membranes. Firstly, a cross-linking modification was performed on polymeric precursors at room temperature before pyrolysis. The effectiveness of chemical cross-linking technology in improving gas separation capability of CMSMs was investigated. In this study, the permeation properties of carbon membranes derived from cross-linked Matrimid were characterized as a function of cross-linking density. Results demonstrated that the permeability of modified CMSMs decreased with increasing in cross-linking density. Detailed examination reveals that cross-linking modification increased the selectivity at a low degree of cross-linking but reduced the selectivity at a higher degree of cross-linking. The improvement of separation efficiency at low degree of cross-linking is presumably related to the swelling of polymer chains by methanol during cross-linking modification. Consequently, the second extremely simple modification method by using pure methanol immersion was developed. It was found that the CMSMs derived from methanol-treated precursors exhibited superior transport properties. Methanol treatment yielded CMSMs with higher selectivities if compared to CMSMs based on untreated and cross-linked Matrimid. Therefore, it can be concluded that the swelling of polymer chains by methanol appears to be an effectual modification method to produce the CMSMs with excellent separation properties.

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Keywords: Carbon molecular sieve membranes; Gas separation; Chemical modification; Cross-linking; Polyimide precursors

1. Introduction

Polymeric membrane separation processes have been developed for large-scale gas separation. It has been identified as an energy efficient and economical tool for gas separation. However, the application of polymeric membranes in rigorous environment has been restricted by their poor thermal and chemical resistances. Moreover, it is arduous for polymeric membranes to breach the trade-off between productivity and selectivity [1,2]. The shortcomings of polymeric membranes have motivated the development of alternative materials for membranes separation in order to conquer the present

challenges and competition in current separation technologies. Therefore, the inorganic membranes with excellent thermal and chemical resistance have come into the contest, where a carbon molecular sieve membrane (CMSM) has observed the high potential for gas separation. CMSMs compare favorably with their polymer precursors by exhibiting intensive gas transport properties. It can achieve higher selectivity without losing the productivity [2–9] and thus surpass the upper bound limit of polymeric membranes. CMSMs have also been recognized with advantages of higher thermal and chemical stability [2,9–13]. This makes CMSMs suitable for corrosive, high pressure and high temperature operation, which is attractive for industrial applications. However the carbon membrane is very brittle and fragile and thus requires more careful handling [8].

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CMSMs are highly porous materials and possess the distribution of small selective pores which similar to the dimension of diffusing gas molecules in the order of 3–6 Å [2,14,15]. Selective adsorption and molecular sieving are the main mechanisms involved in the carbon membrane separation. Their porous nature has led to high permeability, while their molecular sieving morphology restricts a larger degree of rotational freedom of gas penetrants [16]. Therefore, CMSM exhibits high selectivity by permitting effective size- and shape-separation between the gas molecules of similar molecular dimensions. On top of it, the separation capability of CMSM strictly depends on the pores' dimension and surface properties.

Carbonization of polymer precursors has been adopted as a useful method in preparing CMSMs. Many studies have reported that a CMSM with tailored microstructure (pore size, pore volume, etc.) could be obtained by controlling the pyrolysis conditions [2,6,9,13,15,17–19] and post-/pre-treatment conditions [7,10,20–24]. On the other hand, CMSMs can be modified to improve their permeation properties or to solve several problems inherent to their structures. Thus, attention has been focused on the modification of carbon membranes to optimize the separation efficiency. According to reported studies, the current modification technologies performed on carbon membranes are limited to thermostabilization, oxidation and chemical vapor deposition. Primarily, Koresh and Soffer [22] proposed the first modification methods on CMSM, which altered the pore openings by oxidation and sintering. They showed that the permeability of CMSM increased for the oxidized membranes whereas lower permeability was observed for sintered membranes. Besides, Suda and Haraya [23] explored the change of pore dimension of carbon membranes formed by calcinating under mild activation to exhibit excellent selectivity for alkene/alkane separation. On the other hand, Hayashi et al. [24] have successfully controlled the pore sizes and increased the selectivity of carbon membranes by chemical vapor deposition of propylene. Hayashi et al. [20] also performed the oxidation on resulting carbon membranes. They suggested that the oxidation has broadened the pore size distribution which resulted in the increment of permeability accompanied by a slight decline in selectivity. Similar results were observed by Kusakabe et al. [10]. According to their study, oxidation increased the permeances without sacrificing the selectivity of carbon membranes. All above mentioned modifications were carried out on resultant carbonized membranes after pyrolysis, but not on polymer precursors. One study involving modification on polymer precursor has been carried out by Kusuki et al. [21], who thermally treated the precursors (polymeric hollow fibers) in atmospheric air at 400 °C for 30 min before pyrolysis. They showed that the thermostabilization

process strengthens the structure of the precursors in order to withstand the high temperatures during pyrolysis. After that, several researches such as Tanihara et al. [8], Okamoto et al. [7] as well as David and Ismail [12] have also applied thermostabilization in their studies. *To our best knowledge, no investigations have been done on chemical modification and solvent treatment of polymer precursors before pyrolysis.*

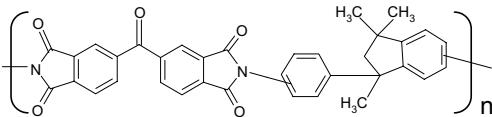
The main objective of this study is to report two novel methods in pyrolyzing the carbon membranes based on modified polyimides in order to improve the separation properties of resultant carbon membranes. These modifications are based on (1) chemical cross-linking and (2) methanol pre-treatment on polymeric precursors. We hypothesize that the space filling by cross-linking reagents during modification may stabilize the structure of the precursor to pyrolysis temperatures. The stable structure of precursors is important to withstand the high temperature pyrolysis because it may prevent (1) the sudden collapse and softening of the polymer chains, (2) preserve a reasonable high interstitial space among chains and (3) somewhat maintain molecular configuration of carbon membranes after pyrolysis. As a result, it is anticipated that the resultant carbon membranes have better gas separation properties after pyrolysis. Since an extremely simple room-temperature cross-linking technology for the modification of polyimide films has been developed by our group for gas separation [25,26], it was employed to test our hypothesis. Similarly, enough data indicate that non-solvent pre-treatment may induce polymer swelling and the pre-treated membranes may have higher free volumes [26]. Thus, attempts are given to investigate if swollen precursors can yield better carbon membranes after pyrolysis.

2. Experimental

2.1. Materials and preparation of polymer precursors

The selection of polymer precursor is an important parameter in determining the separation performance of carbon membranes. Polymers with thermosetting properties, which do not melt and retain its structure during carbonization, are key criteria for carbon membrane materials [9]. In view of this, aromatic polyimides appear as a popular material for the carbonization of carbon membranes due to their superior separation performance and high thermal resistance [6,27,28]. A commercially available polyimide was used as the precursor in this study, which was Matrimid® 5218 (BTDA-DAPI, 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4'-aminophenyl)-1,3-trimethylindane). Table 1 shows the chemical structure and properties of this material.

Table 1
Chemical structure and properties of Matrimid® 5218

Material	Chemical structure	Glass transition temperature, T_g (°C)	Density (g/cm ³)
Matrimid® 5218		323	1.22

Before pyrolysis, polymer precursor was first prepared as dense films. The Matrimid® 5218 powder used in this study was purchased from Ciba Polymers (Hawthorne, New York) and the solvent used for Matrimid was dichloromethane. The polymer was dried overnight at 120 °C under vacuum prior to be used. A 2% (w/w) of polymer solution was prepared by dissolving the polymer powder in the solvent. The solution was then filtered with 1 µm filters (Whatman) and casted onto a wafer plate. The casting process was carried out at room temperature. The polymer films were formed after most of the solvent had evaporated slowly. The nascent films were dried in vacuum at 250 °C for 48 h to remove the residual solvents. Finally, the membrane films with a thickness of about 60 µm were ready for testing, modification and pyrolysis.

2.2. Membrane modification by cross-linking and methanol treatment

For the cross-linking modification, a 10% (w/v) of cross-linking reagent comprising of *p*-xylenediamine in methanol was prepared. The membrane modification was performed by immersing membrane films into the cross-linking reagent for specific durations (1 day or more). The films were then washed with fresh methanol immediately after removal from the reagent solution in order to wash away the residual solution on films, followed by drying naturally at room temperature. The above procedures were repeated by using pure methanol instead of the cross-linking reagent for methanol treatment.

2.3. Preparation of carbon molecular sieve membranes

The pyrolysis was performed by a Centurion™ Neytech Qex vacuum furnace, where polymer precursors were placed on the wire meshes and carbonized under vacuum. The pyrolysis temperature of 800 °C was used in the preparation of carbon membranes for this study. Generally, the final pyrolysis temperature was reached by several steps: the polymer films were heated to 250 °C from room temperature at a rate of 13 °C/min, subsequently the temperature was raised to 750 °C with a heating rate from 2.5 to 3.8 °C/min and then the final temperature was reached at a rate of 0.2 °C/min. The

final temperature was held for 2 h. After completing a heating cycle, membranes were cooled slowly in a vacuum furnace to room temperature. The detailed pyrolysis protocol is illuminated in Fig. 1 and the denomination (ID) of resultant carbon membranes were summarized in Table 2.

2.4. Characterization of carbon membranes

Several characterization instruments were employed to characterize the CMSMs fabricated at different pyrolysis conditions. The elemental analysis was performed with a Perkin–Elmer 2400 Series II CHNS/O Analyzer. This technique determined the presence of elements such as carbon, hydrogen and nitrogen in the materials. The results given in Table 2 are the percentage amounts of these atoms against the total weight. The substances were combusted under an oxygen stream in a furnace at high temperatures (950 °C). The end product of combustion would be mostly the oxides of the concerned elements in the form of gases, such as CO₂, H₂O and N₂. These gases are then separated and carried to a detector using inert gas like helium or argon and the composition was measured as a function of thermal conductivity.

The densities of carbon membranes were measured by a top-loading electronic Mettler Toledo balance coupled with a density kit based on the Archimedes' principle. The samples were first weighed in air and again in a known-density liquid, which was high purity ethanol (99.9%) in this study. The measurements were carried

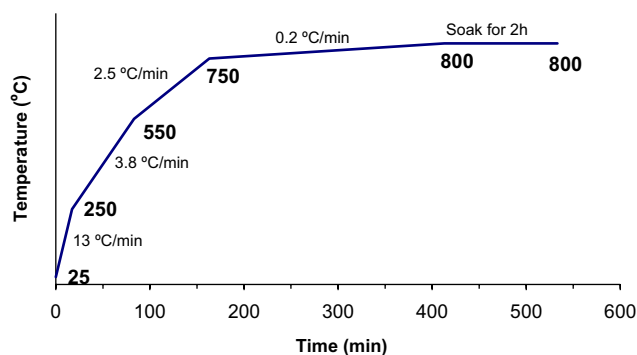


Fig. 1. Steps involved in the pyrolysis process at a final temperature of 800 °C.

Table 2
Elemental analysis of Matrimid precursor and pyrolyzed membranes

Membrane	ID	Elemental content (wt.%)				Ratio		
		C	H	N	O	H/C	N/C	O/C
Precursor	–	76.07	4.39	5.07	14.48	0.058	0.067	0.190
Carbon membrane (CM)	M-CM-800	84.71	2.03	3.15	10.11	0.024	0.037	0.119
CM derived from 1-day cross-linked precursor	M-1xl-800	86.80	1.60	3.09	8.51	0.018	0.036	0.098
CM derived from 3-day cross-linked precursor	M-3xl-800	85.86	1.51	3.09	9.54	0.018	0.036	0.111
CM derived from 7-day cross-linked precursor	M-7xl-800	85.75	1.45	3.14	9.66	0.017	0.037	0.112
CM derived from 1-day methanol-treated precursor	M-MeOH-800	85.89	1.56	2.71	9.84	0.018	0.032	0.114

out at room temperature by the buoyancy method and the density was calculated as follows:

$$\rho_{\text{membrane}} = \frac{w_0}{w_0 - w_1} \rho_{\text{liquid}} \quad (1)$$

where w_0 and w_1 are the membrane weights in air and in ethanol, respectively.

The weight loss of carbon membranes during pyrolysis was characterized by thermogravimetric analysis (TGA) with a TGA 2050 Thermogravimetric Analyzer (TA Instruments). The analysis was carried out with a ramp of 10 °C/min at the temperature ranging from 50 to 900 °C. The purge gas for balance was N₂ and its flow rate was controlled at 50 ml/min. With the aid of a N₂ flow, the exhausted products from TGA were flushed through a transfer line to a gas cell of a Bio-Rad FTS-3500 FTIR spectrometer. The temperatures of the transfer line and the gas cell were maintained at 150 °C to prevent condensation on the windows. The exhausted products were analyzed in a gas cell and the IR spectra were obtained by a KBr beam splitter. With TGA-FTIR, the mass loss throughout the profiles and materials emitted at a particular temperature can be obtained.

Wide-angle X-ray diffraction (WAXD) was performed to quantitatively measure the ordered dimensions and interchain spacing of the carbon membranes with a Bruker X-ray diffractometer (Bruker D8 advanced diffractometer) at room temperature. The d -spacing values indicate the average spacing of the chain center in a polymer matrix. Accordingly, a small piece of sample film was first secured onto a holder. The measurement was completed in a scan range of $2\theta = 2.5$ – 65.4° with a step increment of 0.02° . Ni-filtered CuK α radiation with a wavelength of $\lambda = 1.5418 \text{ \AA}$ was used in the experiments. Average d -spacing was determined based on the Bragg's law.

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

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

Analysis of the CO₂ adsorption isotherm in the carbon material was used to determine the micropore vol-

ume of the material. These measurements were done by a Quantachrome Autosorb-1 Surface Area and Pore Size Analyzer. About 50–100 mg sample was used in the measurement and out-gassed at 300 °C for more than 24 h before testing. The CO₂ adsorption tests were carried out at 0 °C in an ice water isothermal bath. The pores are assumed to have a slit-shaped pore geometry. Therefore, the results were analyzed based on the Horvath–Kawazoe (HK) method. This method enables the calculation of micropores volume from the low relative pressure region of the adsorption isotherm.

2.5. Gas permeation measurements

Membranes were tested in pure gas system. The pure gas permeabilities were determined by the constant volume method. Detailed experimental design and procedures were reported elsewhere [29]. The permeabilities were obtained in the sequence of N₂, CH₄, CO₂ and O₂ at 35 °C and 10 atm. The reason why O₂ was the last gas tested in the permeation measurements is due to the report that carbon surface exhibited the strongest affinity to O₂ even at room temperature [30–32]. Generally, carbon membranes are hydrophobic in nature. However, CMSMs exposed to air/O₂, O₂ would readily chemisorb to the carbon surface and form the carbon–oxygen surface complexes. Unfortunately, this oxygen containing surface acts as primary sites for water sorption and attracts additional water molecules. This process would result in the formation of water clusters through hydrogen bonding. As a consequence, the interaction of O₂ with the carbon surface may reduce the effective size of pores and restrict the diffusion of penetrants, and then diminish the membrane separation capability.

The gas permeability P (in Barrer, 1 Barrer = $1 \times 10^{-10} \text{ cm}^3 \text{ (STP)-cm/cm}^2 \text{ s cm Hg}$) was determined from the rate of pressure increase (dp/dt) obtained when permeation reached steady state. The ideal separation factor of a membrane for gas A to gas B is evaluated as follows:

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (3)$$

3. Results and discussion

3.1. Characterization of carbon membranes

Table 2 presents the elemental analysis of precursor and membranes carbonized from Matrimid® 5218 under vacuum environment. The analysis exemplified that all Matrimid-derived carbon membranes pyrolyzed at 800 °C contained about 85–87% carbon, 1.5–2.0% of hydrogen, 3.0% of nitrogen and 8.5–10% of oxygen. In particular, carbon membranes carbonized from 1-day cross-linked Matrimid exhibited the highest carbon content and the lowest presence of oxygen. Moreover, the most depleted elemental ratio of oxygen to carbon was displayed by M-1xl-800.

The density measurements were performed on precursor and carbon membranes. The results are shown in Table 3. Essentially, the density of membranes increased after pyrolysis. According to the data in Table 3, it seems that cross-linking modification hardly changed the density of resulting carbon membranes. However, the carbon membrane prepared from 1-day methanol-treated Matrimid exhibited higher density than other Matrimid-derived CMSMs. It was possible to speculate that, after the methanol treatment, polymer chains have more freedom to become more orderly and closely packed during the pyrolysis. This result also implied an increment of carbon material per unit volume of carbon membranes for a CMSM derived from the methanol-treated Matrimid.

The weight variation of Matrimid precursors during the heating process was examined by TGA in N₂ atmosphere and illustrated in Fig. 2. Polymers degradation was observed by the TGA curve. Firstly, Matrimid precursors start to decompose at around 500 to 550 °C, and then the weight loss increased abruptly with further increase in temperature. The total weight loss at 800 °C was approximately 50% during the pyrolysis. Inspection of Fig. 2 reflects that the 1-day methanol-treated Matrimid encountered greater mass depletion compared to the original and 1-day cross-linked Matrimid.

Typically, the weight loss of CMSMs during pyrolysis is attributed to the release of compounds from the precursor. The evolution of these compounds was

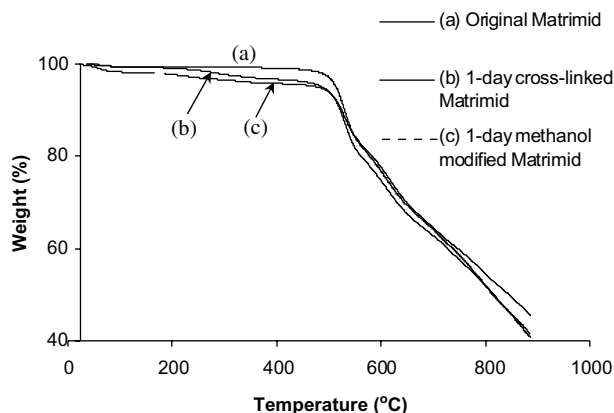


Fig. 2. Thermogravimetric analysis of Matrimid precursors.

monitored by FTIR. Fig. 3 illustrates the general characteristics of the products evolution during degradation. From the membrane thermogram, at temperatures below 200 °C, a small mass decrement, which resulted from water evolution, was detected. During 350–450 °C, polymer degradation began, and few volatile compounds were observed due to the evolution of CO₂ (its characteristic band is at around 2350 cm⁻¹), aromatic ring stretching vibrations (–C=C–) represented by the bands around 1600 cm⁻¹ and stretching of free O–H in the range of 3500–3800 cm⁻¹. However, the bands at 3500–3800 cm⁻¹ do not represent the existence of H₂O without the corresponding H₂O bands around 1630 cm⁻¹. Subsequently, the weight loss became significant after 500–550 °C, where polymers degraded distinctly to form a graphite-like structure. At this temperature range (500–550 °C), the following characteristic bands appeared: free O–H stretching, CO₂ band, CO at its characteristic double bands (2170 and 2110 cm⁻¹) at the right wing of the CO₂ 2350 cm⁻¹ band, aromatic ring vibrations and aromatic =C–H out of plane deformation vibrations at 671 cm⁻¹ (most likely by benzene), 3100 cm⁻¹ band ascribed the C–H stretching, a band of aromatic ethers (=C–O–C stretching) at 1310 cm⁻¹ and NH₃ (double bands at 965 and 930 cm⁻¹). Furthermore, examination on Fig. 3(a) and (b) revealed the similarity of the products evolution between unmodified and cross-linked Matrimid during degradation. Crucially, however, there was a striking distinction occurred at 550 °C, the 1627 cm⁻¹ band represents the deformation vibration of the primary amine N–H, which was observed for the 1-day methanol-treated Matrimid (Fig. 3(c)). Unfortunately, the evolution of O₂, N₂ and H₂ from the polymer during the pyrolysis, as commented by other studies [17,21], could not be monitored by FTIR. However, it was certainly true that the thermal degradation of polyimides during pyrolysis produced CO₂, CO, O₂, N₂,

Table 3
Density of carbon materials

Matrimid membranes	Density (g/cm ³)
Precursor	1.22
M-CM-800	1.48
M-1xl-800	1.49
M-3xl-800	1.49
M-7xl-800	1.49
M-MeOH-800	1.51

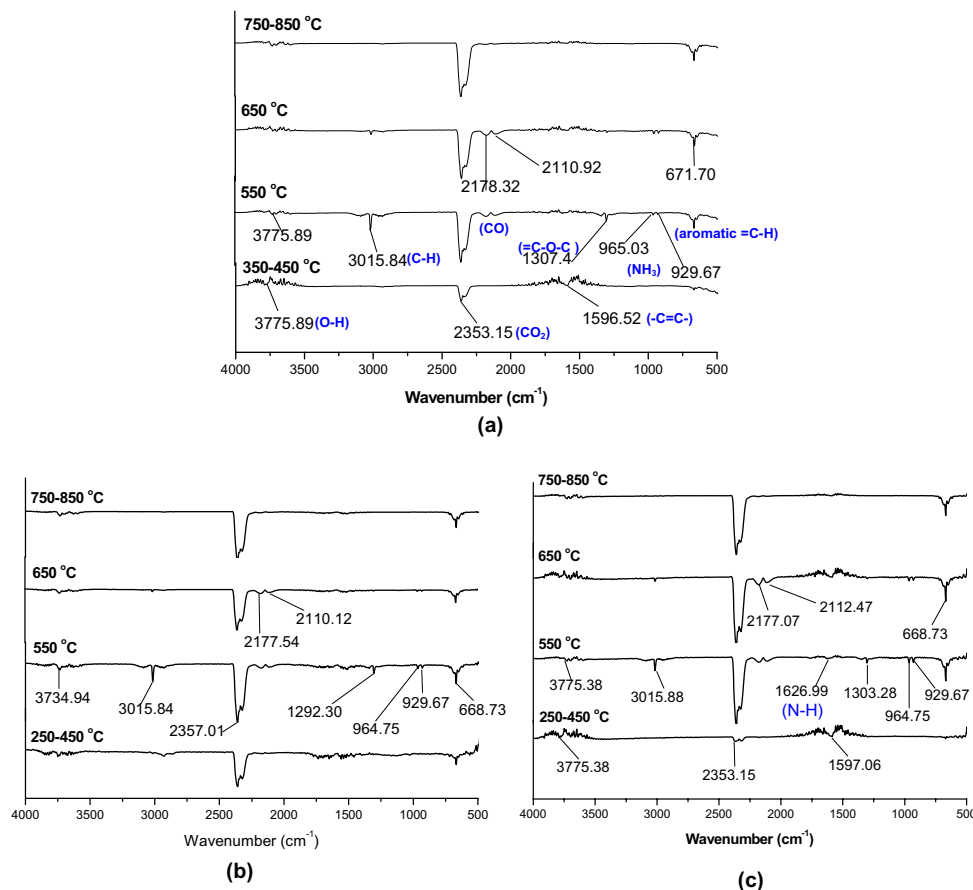


Fig. 3. Selected IR spectra of the TGA products for (a) original Matrimid precursor, (b) 1-day cross-linked Matrimid and (c) 1-day methanol modified Matrimid.

NH_3 , benzene, phenyl, aliphatic hydrocarbons and other aromatic compounds, which is in line with the reported literature [17,21,33].

Fig. 4 shows the d -spacing values of Matrimid® 5218-derived CMSMs determined from the diffraction peak angles. For amorphous polymer precursor, Matrimid possessed a d -spacing value at 5.6 Å. According to Fig. 4, the d -spacing peak of Matrimid shifted to 3.7 Å, which is approximate the size of penetrants used in this study (nitrogen, oxygen, methane and carbon dioxide) after pyrolysis at 800 °C. In addition, this d -space value further decreased to 3.6 Å for both CMSMs derived from cross-linked and methanol-treated Matrimid. Besides, a sharper peak obtained at around 20 Å indicative for increased regularity and packing order of CMSMs compared to its polymer precursor. Prominently, a new peak was perceived for CMSMs at around 2.1 Å. This result demonstrated the carbon-carbon spacing, which is recognized by d -spacing in graphite planes. Similar results have been reported elsewhere [1,2,17]. Hypothetically, the conjugate aromatic graphitic structure was formed and CMSMs show the graphite nature of high selectivity.

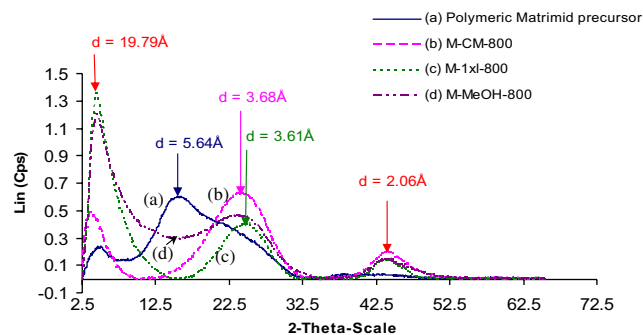


Fig. 4. Wide-angle X-ray diffraction of CMSMs derived from Matrimid® 5218.

3.2. Effects of pyrolysis on gas permeation properties

Pyrolysis was performed on Matrimid at 800 °C under vacuum environment. The gas permeabilities and ideal selectivities of O_2 , N_2 , CO_2 and CH_4 through CMSMs derived from Matrimid are summarized in Table 4. The pyrolysis was found to have great effects on the separation capability of membranes. The gas

Table 4

Gas separation properties of Matrimid precursor and carbon membranes

Membrane	Permeability (Barrer)				Ideal selectivity		
	CO ₂	O ₂	N ₂	CH ₄	O ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
Precursor	6.5	1.68	0.25	0.19	6.6	34	26
M-CM-800	611	227	30.3	10.0	7.5	61	20
M-1xl-800	609	179	27.6	8.2	6.5	78	23
M-3xl-800	459	149	22.9	8.0	6.5	57	20
M-7xl-800	319	118	18.5	5.7	6.4	56	17

permeabilities of Matrimid-derived carbon membranes pyrolyzed at 800 °C increased dramatically after carbonization compared to their polymer precursor. It is undoubtedly that pyrolysis effectively produce the separation membranes with high industrial value, especially for Matrimid having the low permeability for its polymeric membrane. Simultaneously, the selectivities of O₂/N₂, CO₂/CH₄ improved after pyrolysis. This implies that CMSMs possessed molecular sieve properties by exhibiting extremely high permeability and selectivity compared to the permeability and selectivity achieved by the Knudsen diffusion. Accordingly, pyrolysis resulted in amorphous carbon materials containing micropores. Therefore, the main mechanism involved in the gas transport through CMSMs is molecular sieving, where the membranes can effectively discriminate gas molecules with similar molecular sizes. As compared to the selectivity of O₂/N₂ and CO₂/N₂ pairs, the degree of increment was higher for CO₂/CH₄, probably due to a greater difference in molecular sizes of CO₂/CH₄. In this case, separation can effectively achieved when CO₂ with a smaller kinetic diameter is able to access the small pore mouths and diffuses through CMSMs while retaining the bigger CH₄ molecules. The results suggest that the separation of CO₂/CH₄ becomes more pronounced for Matrimid-derived CMSM pyrolyzed at 800 °C under vacuum environment. On the other hand, Fig. 5 depicts the behavior of pure gas permeabilities of Matrimid-derived CMSMs with the kinetic diameter of gas molecules. The permeabilities of CMSMs were in the order of CO₂ (3.3 Å) > O₂ (3.46 Å) > N₂ (3.64 Å) > CH₄ (3.8 Å), where permeability is decreasing in the order of increasing gas kinetic diameter.

3.3. Effect of the degree of cross-linking the on gas permeation properties of CMSMs derived from Matrimid precursor

Fig. 5 shows the permeation properties of carbon membranes based on cross-linked Matrimid with different immersion times. It is obvious that the permeability of CMSMs decreased with increasing the cross-linking density. Besides, Fig. 6 describes the effect of immersion time on the ideal gas selectivity of resultant CMSMs and reveals that the maximum selectivity was

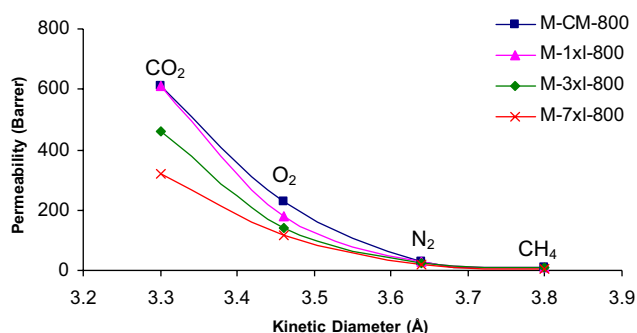


Fig. 5. Gas permeabilities of Matrimid-derived CMSMs vs. kinetic diameters of gas molecules.

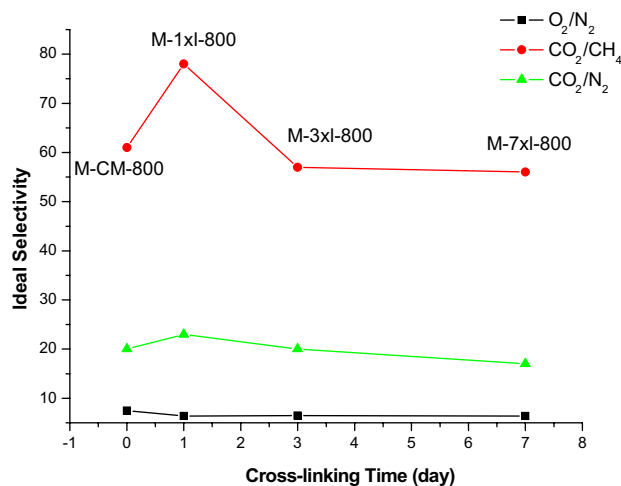


Fig. 6. Effect of immersion time on the ideal gas selectivities of Matrimid-derived CMSMs.

attained by CMSMs pyrolyzed from the 1-day cross-linked Matrimid, but selectivities deteriorated at a higher degree of cross-linking. This maximum separation efficiency of M-1xl-800 was presumably relevant to the swelling effect of methanol on polymer precursors during the cross-linking modification, as reported in our previous study about chemical cross-linking on Matrimid [26]. One point which should be addressed here is that the swelling of Matrimid films in the *p*-xylenediamine methanol solution is a pre-requisite for the formation of cross-linking. According to our previous

study [26], it cannot be denied that the swelling of polymer chains by methanol plays a predominant role at a low degree of cross-linking, which occurred at 1-day immersion time. This leads to the conclusion that reduction in free volume, chain mobility and the interstitial space among chains during cross-linking modification on polymer precursors is an ineffective technology in producing high separation performance CMSMs. While it may be true to some extent, the swelling of polymer chains by methanol may be an effectual modification method to produce the CMSMs with excellent separation properties, which will be discussed in the next section.

3.4. Permeation properties of CMSMs based on the methanol modified polyimides

As previously mentioned, with inspiration from the swelling effect during the cross-linking modification, a novel modification on polymer precursors was performed by immersing the polymer films simply in methanol for 1-day. The dried methanol-treated polyimide films were then carbonized at 800 °C under vacuum environment, and their permeation properties were characterized after pyrolysis.

Table 5 lists the gas permeabilities and ideal selectivities of CMSMs derived from Matrimid precursors. As compared to the selectivities of original carbon membranes, selectivities remarkably improved for CMSM derived from the methanol-treated precursor, which is best observed for the gas pair of CO₂ and CH₄ because of the large difference in their molecular sizes. The permeabilities, however, decreased after the methanol modification. For Matrimid-derived CMSMs, the highest selectivities were achieved for M-MeOH-800 compared to the original carbon membranes and the carbon membranes derived from 1-day cross-linked precursor. This is an indication that the swelling of polymer precursors before pyrolysis has a significant effect on separation properties of the resultant CMSMs. According to our previous study on the occurrence of swelling by methanol on the Matrimid precursor [26], it was found that the permeabilities of gases increased tremendously, from a minimum of 50% to a maximum of 106% for films immersed in pure methanol for 1 day. It may well be the case that the swelling of polymer by

methanol induced chain mobility, as well as increased the interstitial space among the chains. As a consequence, polymer degradation might occur more readily with structural organization during carbonization after swelling as compared to untreated and cross-linked precursors. Fig. 2 demonstrates that the 1-day methanol-treated Matrimid encountered greater mass depletion compared to the original and 1-day cross-linked Matrimid, and there was an additional N–H functional group detected by FTIR (Fig. 3(c)) for the 1-day methanol-treated Matrimid during thermal degradation. This clearly indicates that the high mobility of polymer chains resulted from the methanol treatment gave rise to the ease of structural organization and created smaller selective micropores, which yielded the highest selectivity CMSM with the lowest flux. The micropore volume and pore size distribution determined by the analysis of CO₂ absorption isotherm pointed out that the micropore volume of M-CM-800 (0.07141 cc/g) was smaller than that of M-MeOH-800 (0.07917 cc/g). Moreover, carbon membranes prepared from the 1-day methanol-treated precursor exhibited a higher density than original carbon membranes, as shown in Table 3. Therefore, it is possible to argue that the structure of carbon membrane obtained from the methanol-treated precursor was denser and more orderly packed.

It can be concluded that the swelling of polymer chains by methanol plays an important role in altering the separation efficiency of CMSMs. Apparently, it is perceptible that methanol treatment had an imperative effect in altering the density, weight reduction and pore size distribution of resultant CMSMs. In order to have a clearer picture on the effect of polymer swelling on resultant CMSMs, sorption experiments will be carried out in a future study in order to investigate the transportation of gas molecular via CMSMs.

Finally, as Matrimid-derived CMSMs exhibited the excellent separation properties for CO₂/CH₄, the CO₂/CH₄ trade-off lines for polymer precursor and pyrolyzed membranes are shown in Fig. 7. It is clear that both the permeability and selectivity of membranes are well-above the upper-bound curve after carbonization, especially for those pyrolyzed under optimum conditions such as CMSM derived from the methanol-treated polymer. Since it is very difficult to synthesize or develop a new polymer material having properties beyond the trade-

Table 5
Gas separation properties of CMSMs derived from methanol-treated Matrimid

Membrane	Permeability (Barrer)				Ideal selectivity		
	CO ₂	O ₂	N ₂	CH ₄	O ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
M-CM-800	611	227	30.3	10.0	7.5	61	20
M-1x1-800	609	179	27.6	8.2	6.4	78	23
M-MeOH-800	423	138	15.8	4.8	8.8	88	27

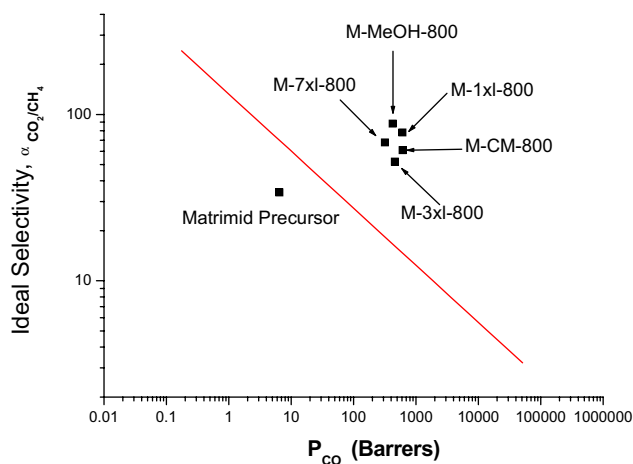


Fig. 7. Separation properties of CO_2/CH_4 for Matrimid-derived CMSMs and precursor with respect to the upper-bound curve.

off line, CMSM appears to be an extremely attractive candidate for future gas separation technology.

4. Conclusion

Carbon molecular sieve membranes in this study were derived from a polyimide Matrimid® 5218 precursor. Several characterization instruments such as Elemental Analysis, TGA-FTIR, XRD, Density Balance and Pore Size Analyzer were employed to characterize the CMSMs. The pure gas permeabilities were determined by constant volume method. The permeabilities of CMSMs decreased in the order of increasing gas kinetic diameters, $\text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{CH}_4$. On the other hand, a room-temperature cross-linking modification was performed on Matrimid® 5218 by immersing the films in a 10-w/v % of *p*-xylenediamine methanol solution for specific durations. CMSMs were then carbonized from cross-linked Matrimid at 800 °C under vacuum environment. The effect of cross-linking modification on the resultant carbon membranes was investigated. The permeability of CMSMs derived from cross-linked Matrimid decreased with cross-linking density while the maximum selectivity was attained for CMSMs pyrolyzed from 1-day cross-linked Matrimid. The results suggested that the selectivity increased at a low cross-linking density but decreased at a high degree of cross-linking. Detailed examination reveals that the swelling of polymer chains during cross-linking modification at a low cross-linking density is the possible reason resulting in the increment of selectivity. Consequently, the Matrimid precursor was treated in pure methanol before pyrolysis in order to examine the effect of polymer chains' swelling on resultant CMSMs. It appears that methanol treatment significantly improved the selectiv-

ity of resultant carbon membranes. This is probably due to the high mobility of polymer chains resulting in the ease of structural organization and creation of smaller selective micropores. Therefore, it underlines the importance of the swelling effect on polyimide precursors, where swelling by methanol emerged as an effective modification method in producing CMSMs with excellent separation capabilities when compared to the chemical cross-linking modification.

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