Polyimide-Carbonized Membranes for Gas Separation: Structural, Composition, and Morphological Control of Precursors

Pei Shi Tin[a]; Youchang Xiao[a]; Tai-Shung Chung[a]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore

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Department of Chemical and Biomolecular Engineering, National
University of Singapore, Singapore

Abstract: It is widely accepted that the characteristics and separation performance of carbonized membranes can be optimized by controlling the parameters of pyrolysis protocol. In spite of this, plenty of research studies have pointed out that the chemical composition and moiety geometry, chain rigidity and structure, and physicochemical properties of polymeric precursors play major roles in determining the properties of the resultant pyrolytic membranes, especially the micro-pore structure and separation capability. Therefore, the morphological, structural and microphase control of the polymeric membranes are the essential keys to fabricate highly permeable and selective carbon membranes. This review paper aims to give an overview about the precursor materials aspects, preparations and their influence on the separation properties of carbon molecular sieve membranes (CMSMs). The evolution of membrane structure and separation performance from the state of polymer to carbon is also included. The subjects covered in this review paper intend to provide in-depth understanding and insights to membranes' researchers with effective preparation of CMSMs from the precursor's point of view.

Keywords: Carbon molecular sieve membranes, polyimide, chemical structure, membrane transformation, gas separation

INTRODUCTION

The ever-increasing of energy consumption for conventional separation technologies in chemical and petrochemical industries has become a major concern due to global resource depletion. Besides, with their adverse impacts on the environment and high operating costs, researchers were motivated to seek for alternative techniques that are more economical, energy-efficient and environmental friendly. As a consequence, membrane-based separation has rapidly grown from being a laboratory curiosity to becoming a commercially viable separation approach within the last two decades (1). A large-scale membrane-based gas separation system alone or in hybrid systems with other methods has become the standard separation processes in many industrial sectors.

Today, polymeric membrane separation processes, which are extremely economically attractive, are widely used in different gas separation processes. However, compared to inorganic materials, polymers have relatively poor chemical and thermal resistances, and tend to densify with time; therefore, the separation performance of polymeric membranes commonly declines with a passage of time. The application of polymeric membranes in high pressure and rigorous environment, such as an atmosphere having heavy hydrocarbons, aromatics and polar solvents has thus been restricted. In addition, it is also arduous for polymeric membranes to breach the tradeoff between productivity and selectivity (2). This limitation is probably due to the fact that the separation of a non-polar gas by polymeric membranes through the solution-diffusion mechanism is mainly based on the molecular size, resulting in limited selectivity especially for gases with similar molecular dimensions. Obviously, seeking for more stable materials that are highly permeable and selective is the immediate task for membrane researchers. In response to the demand for new materials, carbon molecular sieve membranes (CMSMs), inorganic membranes have emerged as very promising materials for gas separation.

Carbon molecular sieve membrane-based separation, an energy-saving technology, had rapidly received global attention due to the superior separation properties (3, 4). There is growing interest in using CMSMs for the separation of organic vapor mixtures and gases with similar molecular sizes. CMSMs obtained from the pyrolysis of polymeric materials have shown permeation properties exceeding their polymeric precursor membranes. They can achieve higher selectivity without losing productivity (5–7) and thus surpass the upper bound limit of polymeric membranes. Most importantly, CMSMs present the advantages of excellent chemical and thermal stability (8–11). Furthermore, CMSMs derived from the pyrolysis of polymeric precursors offer a very distinctive feature, where the final membrane's morphology and microstructure can be tailored to obtain desirable permeation properties (11, 12). These unique characteristics make them potentially attractive for many aggressive industrial applications, such as natural gas processing, enhanced oil

recovery, separation of hydrogen from gasification, the upgrading of biogas and landfill gas, flue gas treatment, purification of methane, separation of olefin/ paraffin, membrane reactors and fuel cells, etc (7, 9, 13–15).

Nevertheless, carbon membranes are very brittle and require more careful handling (11, 12). This makes them difficult to package for module preparation if the membrane surface become larger. Another drawback of carbon membranes is their broad distribution of pore size, as they always possess a nonhomogeneous pore system, consisting of relatively wide openings (6–20 Å) with small selective pores (3–6 Å) (16). It is challenging to produce the CMSMs with very narrow pore size distribution, even by careful control of pyrolysis conditions. The above problems notwithstanding production may be improved to a certain extend by the optimization of precursors selection and preparation. Besides, it is important to point out that the very high production cost of CMSMs has restricted their immediate application in separation tasks. The cost per unit of membrane area for carbon membranes is between one to three orders of magnitude greater than polymeric membranes (17). To overcome these issues, carbon molecular sieve membranes are under intensive investigations by membrane researchers from both academia and industry, especially to optimize the membrane performance for commuting the high production cost.

A substantial amount of information has been published on the gas separation technology by CMSMs. Recently, Ismail and David reviewed the latest developments of carbon membranes for gas separation and their future direction (5). Also, Saufi and Ismail also presented an overview regarding the general fabrication aspects of carbon membranes (18). The aim of this paper is different from the others, and is meant to provide the update on the carbon membranes derived from polyimide precursors. We put specific emphasis on the precursor's influences on the characteristics of the resultant carbon membranes. Based on the theories about the transformation of polyimide precursors to carbon membranes during the pyrolysis process, this review focuses on the effects of precursor chemistry and molecular structures, sample preparation, additives and post-treatment on the separation capability of CMSMs. Hence, we believed that this work can provide insight into the engineering and molecular design of carbon membranes for effective gas separation.

POLYIMIDE—AN IDEAL PRECURSOR FOR CARBON MOLECULAR SIEVE MEMBRANES

Numerous materials and fabrication methods have been adopted by membrane researchers to prepare carbon molecular sieve membranes. Nonetheless, carbon membranes can essentially be prepared through the carbonization or pyrolysis of carbon containing materials, for instance thermosetting resins/ polymers, graphite, coal, pitch and plants (12). Pyrolysis of these materials is generally carried out under vacuum or inert environment, depending on

the membranes properties required. The controlled activation by oxidation is required when natural precursors are used (19, 20). By using polymeric precursor, membrane configurations could be designed and constructed before the carbonization. Therefore, the good processability of polymeric precursors has made them become the major raw materials for carbon membrane preparation. Most importantly, pyrolysis of polymeric precursors produces highly pure carbonaceous membranes with relatively low organic contaminants (21, 22).

The selection of polymeric precursor is a primary factor in carbon membrane preparation, given that although the same pyrolysis conditions have been used, different precursors will result in dissimilar carbon membranes (4). Principally, polymers for CMSMs need to have somewhat thermosetting characteristics that can withstand the high temperature treatments and without softening and decomposing rapidly and suddenly. They must retain their structural shape when heating at any stage of pyrolysis (23–25). A desirable precursor material with the above characteristics is essential to produce crack-free CMSMs (26). Leaky CMSMs often result from the pyrolysis of poor precursors, which decompose rapidly and suddenly with the creation of cracks or large pores. Many thermostable polymers including polyfurfuryl alcohol (PFA) (27–29), polyvinylidene chloride (PVDC) (3, 30), cellulose (31, 32), phenolic resins (10, 33, 34), poly-acrylonitrile (PAN) (35, 36), polyetherimides (7, 23, 37, 38) and polyimides (4, 22, 24, 39–52) were used for the production of carbon membranes.

Among these polymers, the aromatic polyimide-type polymer appears to be one of the most promising materials to yield CMSMs with superior separation properties (4, 38–39, 48). Partly due to its incredible nature of strong and astounding heat and chemical resistance, the configuration of membranes prepared by polyimide precursors can be maintained very well during the high-temperature pyrolysis. Also, aromatic polyimides with high carbon content produce carbon membranes with high carbon yields. Most significantly, polyimides exhibit the graphitization characteristics, which can potentially produce graphitized films with fairly high crystallinity while sustaining their structural shapes after high-temperature carbonization (53). Hence, polyimides have been studied extensively in the preparation of CMSMs in recent years.

TRANSFORMATION OF POLYIMIDE TO CARBON MATERIALS DURING PYROLYSIS

In the production of carbon membranes, pyrolysis is a process in which the polymeric precursors are heated to a high temperature with appropriate heating rates and soak time in a controlled atmosphere (vacuum or inert environment) to produce highly microporous carbon membranes and exhibit the molecular sieve characteristic (54). Unfortunately, the evolution of

polymer precursor to carbon membranes and the change of pore structure in carbon membranes during pyrolysis are complicated and remain unclear.

Hatori et al. investigated the pyrolysis mechanism of Kapton-type polyimide through the analysis of volatile compounds acquired from TGA-GC/MS and hydrolysis methods to selectively break up the polyimide char into low molecular weight compounds (53). Their findings indicate that imide ring cleavage occurred at $500-600°C$, and various intermediates on aromatic segments were generated by hydrogen transfer. A recent study had been performed by Barsema et al. to inspect the intermediate pre-carbonized membranes based on Matrimid polyimide (55). This study focused on the evolution of polymer structures between the annealing and carbonization. During the intermediate state, the decomposition of polymer begins, where the polymer structure ruptures without forming a carbon structure. Barsema et al. concluded from the TGA, FTIR and XPS data that no thermal decomposition occurred at below $425°C$, the polymer underwent physical aging (annealing) and concurrently formed weak charge transfer complexes (CTC). In particular, heat treatment below T_g initiated the polymer densification. Further heat treatment above T_g resulted in a denser chain packing, higher concentration of CTCs and hence the depression of permeability. Once the polymer has been exposed to a temperature above $475°C$, the drastic increase in permeability was observed, due to the onset of thermal decomposition and transition to carbon material. The thermally treated polyimides carry advantageous properties, as plasticization by propylene can be effectively suppressed by heat treatment above T_g.

A comparative study were done by Shao et al. to investigate the intermediate structure of fluoro-polyimide, whose T_g ($425°C$) in the range of the intermediate stage defined previously (56). The evolution of physicochemical and transport properties of membranes from polymeric, intermediate to carbon stages is the focal point in this study. Authors pointed out that the configurational reorganization of membranes and pore size distribution are appreciably affected by T_g, especially at the intermediate stage. The evolution of membrane structure and separation properties of 6FDA-durene during carbonization was explored and summarized as follows:

1. $T < 400°C$: The 6FDA-durene is stable in an amorphous structure. No visible changes were observed for the FTIR-ATR spectra of membranes between $250°C$ and $400°C$, as shown in Figure 1. However, a small weight loss was observed for membranes at this temperature from the TGA thermogram.
2. $400°C \leq T < 450°C$: Polymer starts to transform from its amorphous state to an intermediate structure. At this state, polymer is thermally expanded with a slight increase in thickness and d-spacing value, as illuminated in Figure 2a.
3. $450°C \leq T < 500°C$: 6FDA-durene encounters notable changes in chemical composition, where the increment in the polymer chain mobility accompanied by high degradation rates is detected. As

indicated by the TGA-FTIR data in Figure 2b, the CHF_3 (at 1151 cm^{-1}) start releases at about 450°C. Thus, the scission of CF_3 dominates with insignificant degradation of imide groups at this intermediate stage.
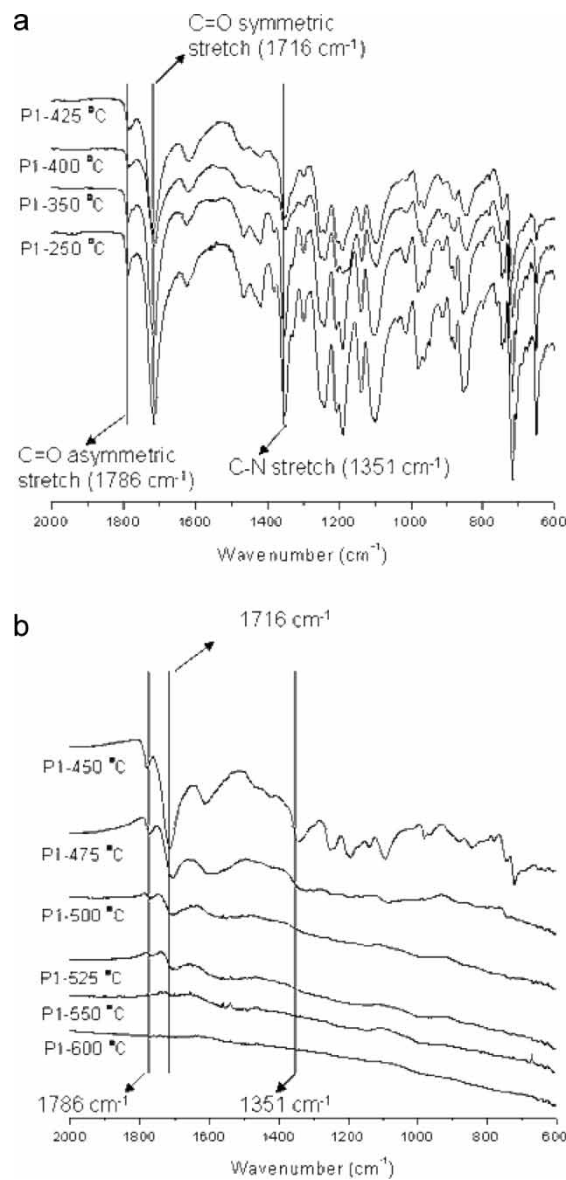
Figure 1. FTIR-ATR of 6FDA-durene membranes treated at different temperatures (a) between 250 and 425°C, (b) between 450 and 600°C.

4. $500°C \le T < 550°C$: Polymer experiences a maximum decomposition rate and significant physicochemical development, which is crucial for the structure transition and pore formation. The degradation of polymer is governed by the transformation of imide groups. This is confirmed
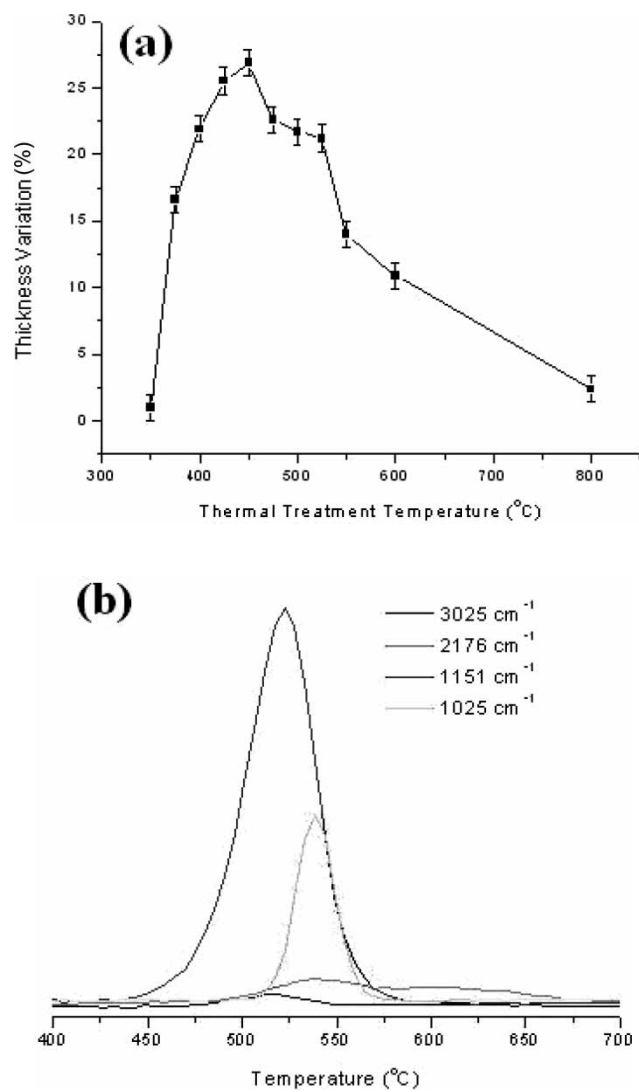
Figure 2. (a) Thickness variation, (b) the evolution of a specific spectra's intensity, (c) the change of gas permeability, and (d) the variation of ideal gas selectivity during 6FDA-durene decomposition.

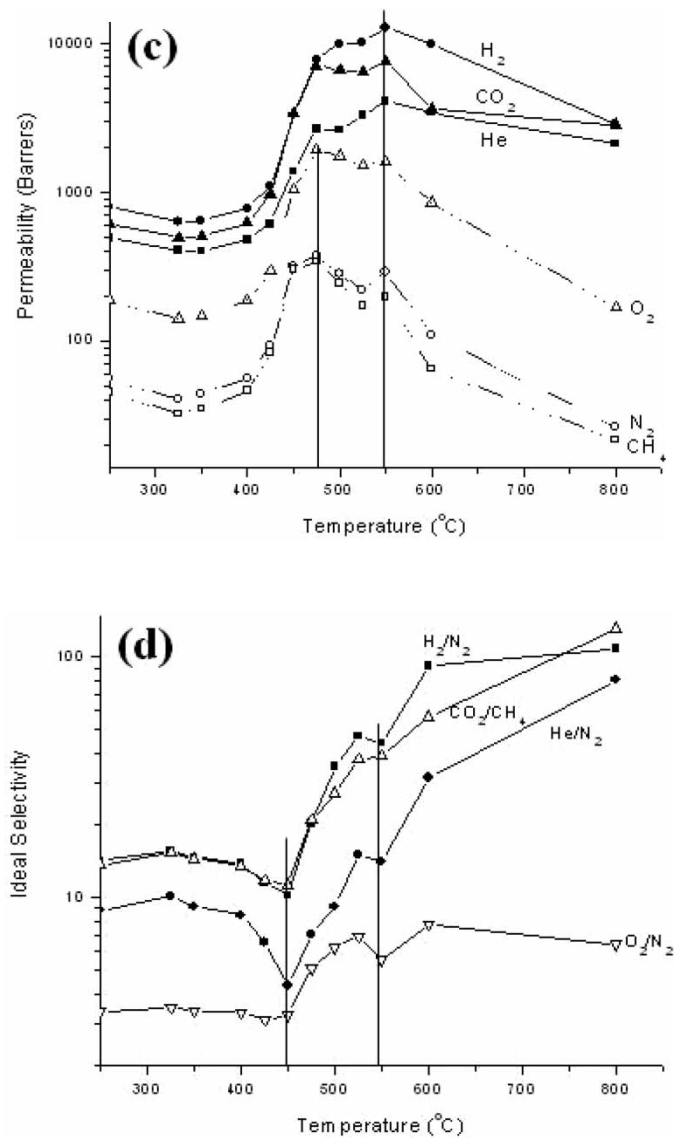*Figure 2.* Continued.

by the decline intensity of imide group during the heat treatment at 450–500°C, as illustrated in Figure 1.

5. T > 550°C: The degradation rate of polymer becomes relatively low and the carbonized membranes transform toward graphite structure with continuous pore shrinkage via structural adjustment. This is consistent with a decline in d-spacing value at the carbon stage.

On the other hand, the pure gas permeation measurement was performed to study the transport properties of polymeric, intermediate and carbon membranes derived from 6FDA-durene. As shown in Figure 2c, the maximum permeability for light gases (He, H_2, CO_2) is obtained at carbonized stage (around 550°C) due to the maximum decomposition rate as well as accelerated pore evolution, whereas the enhanced chain mobility leads to the maximum permeability for medium gases (O_2, N_2, and CH_4) at the intermediate stage. For the same reasons, the lowest selectivity occurs at the temperatures of 450°C and 550°C, as shown in Figure 2d.

Fuertes and Centeno believed that the cross-linking of polymer chains during pyrolysis would cause the formation of disordered pores structures (24). On the other hand, some researchers proposed that the resultant CMSMs possess an amorphous microporous structure created by the evolution of gases as a result of molecular and structural rearrangements of the starting polymeric precursor during the pyrolysis process. Specifically, the weight loss of membranes after pyrolysis is attributed to the release of ammonia (NH_3), hydrogen cyanide (HCN), methane (CH_4), hydrogen (H_2), nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), benzene, phthalimide and others during thermal degradation of polymer (57–60).

Mariwala and Foley have offered insight into one possibility for the pore formation during polymer pyrolysis (60, 61). According to their examination on pyrolysis, the polymeric precursor decomposed at a temperature range of 200–500°C accompanied with the formation of highly chaotic structure consisting of amorphous carbon and microdomains. As schematically illustrated in Figure 3, the chaotic structure of carbon material is viewed as a distribution of carbon in graphitic and amorphous microdomains. At this stage, fairly large pores surrounded by amorphous and crystalline-like regions are observed in the membrane. As a result, this kind of carbon materials has very high gas permeability but poor gas selectivity. The chaotically arranged graphitic microdomains are embedded in non-graphitic or amorphous carbon, where the carbon material is in a non-equilibrium state. Hence with raising the pyrolysis temperature or increasing soak time, the size of aromatic microdomains increases at the expense of amorphous carbon regions. A more ordered structure will be formed, and the average pore mouth dimension decreases in size. Consequently, the gas permeability of carbon membranes decreases and gas selectivity increases with an increase in pyrolysis temperatures. The internal growth of aromatic microdomains will continue with further increase in pyrolysis temperature or thermal soak time, where the micropores would gradually collapse as the microdomains completely align with one another. To avoid the significant loss of the separation capability of carbon material at an elevated pyrolysis temperature, and balance between the permeability and selectivity, an optimum temperature must be determined.

As mentioned previously, the chemical composition and thermal history of carbon precursors, pyrolysis conditions, as well as pre/post-treatment are the factors that determine the microporosity population formed in carbon
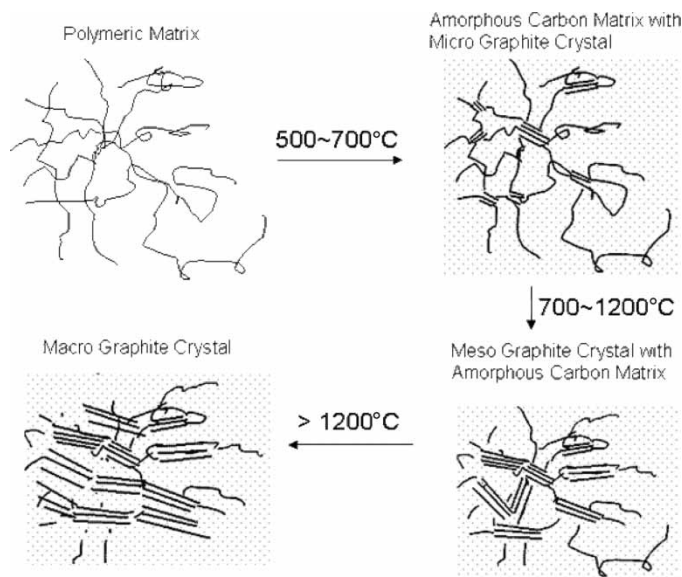
Figure 3. Conceptual model for "pore" structure evolution and reorganization from polymer to carbon.

matrix. During pyrolysis, the polymer chains may cross-link at low temperatures (approximately at a temperature above T_g, but below the degradation temperature). The pyrolysis pathway and degree of cross-linking are governed by the chemical composition and molecular structure of polymeric precursors. The degree of cross-linking in this stage is important in controlling the membrane morphology and the extent to which the non-uniform or amorphous carbon will convert to aromatic microdomains at higher temperatures (61). The cross-linking of polymer chains during pyrolysis also prevents the formation of large graphite-like crystals but induces formation of disordered structures (24). This is due to the fact that the cross-linked structures are strong and stable bonds, which may kinetically prevent structural transformation and frozen carbon atoms movement. Once the pathway to graphite is blocked, the microdomains are unable to convert to graphitic carbon easily even at high temperatures.

INFLUENCE OF POLYMERIC PRECURSOR ON THE CHARACTERISTICS OF CARBON MEMBRANES

As stated previously, CMSMs are fabricated through the carbonization/ pyrolysis of pre-existing polymeric precursors. The thermal degradation of polymers and misalignment of aromatic microdomains of the starting
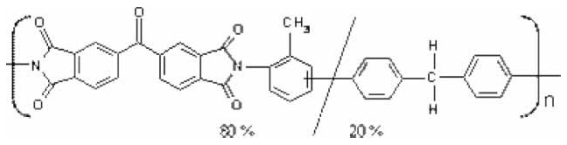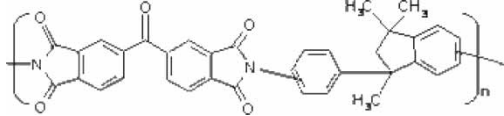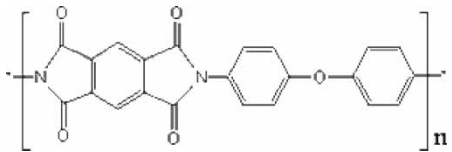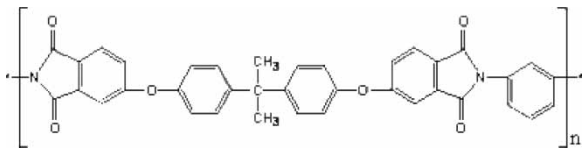
polymeric precursor during carbonization are the main causes for the formation of void spaces in the carbon matrix. Many studies show that the pyrolysis conditions and precursor chemistry impose significant effects on the gas permeation properties of a CMSM. Pore dimensions and their distribution in the microstructure are not only strongly dependent upon the pyrolysis protocols and environments, but are also affected by the choice and preparation of polymeric precursors. The chemical composition and thermal history of carbon precursors, especially, are two of the important factors that determine the pore's population formed in the carbon matrix. Thereby, it is worthy to examine the influence of polymeric precursor on the characteristics of the resultant carbon membranes. In this paper, we reviewed the effects of chemical structures, blended polymer precursors, additives/fillers and pretreatment of polyimides on the structural and separation properties of CMSMs.

Effects of Chemical Structure of Polyimide as Carbon Membrane Precursors

Polyimides are versatile plastics as they are prepared from a variety of dianhydride and diamine monomers, characterized by repeating imide structural units in the polymer backbone (62). The identical pyrolysis protocol may result in different morphologies and separation properties for different polyimides-derived carbon membranes. It is certainly true that the morphology and physical properties of precursor membranes appreciably affect the permeation properties of a carbon membrane. Indeed, materials selection and fabrication is important to pattern the membranes with suitable properties for a specific separation task through an appropriate technique.

In our previous work, we have compared the gas separation performance of CMSMs derived from four commercial polyimides: P84, Matrimid, Kapton and Ultem (polyetherimide) (68). The chemical structures and properties of four polyimides are shown in Table 1. Among these polyimide-derived carbon membranes, we have prepared P84 and Matrimid-derived carbon membranes in our lab. Under the identical pyrolysis conditions (i.e., 800°C under vacuum environment), the carbon membrane derived from the Matrimid precursor is more permeable but less selective than the P84-derived CMSM. This arises from the fact that P84 precursor possesses smaller d-space values and FFV, where its polymer chains are more tightly packed as compared to the Matrimid precursor. Besides, Kapton-derived CMSMs were investigated by Feurtes et al. (49), Suda et al. (4, 69) and H. Hatori et al. (51, 70). The membrane carbonized from Kapton film at 800°C under vacuum (4) exhibited relatively low permeability but higher selectivity than the former two polyimides-based CMSMs. Lastly, supported Ultem carbon membranes on porous substrates were prepared by Sedigh et al. (7, 37), Fuertes and Centeno (23), while the Ultem carbon hollow

Table 1. Chemical structures and properties of commercially available polyimides

Materials	Chemical structure	$T_g(^\circ C)$	FFV	Density (g/cm^3)
P84		315	0.136	1.31
Matrimid 5218		323	0.169	1.22
Kapton		360−410	0.105	1.42
Ultem		215	0.135	1.28

fiber was studied by Coutinho et al. (38). Fuertes and Centeno's Ultem carbon membrane had CO_2/CH_4 separation factor of 25 tested at $25°C$, which is very small compared to the selectivity of other polyimides-based CMSMs. Even though it is inappropriate to direct compare their permeation properties with others because of different configuration and pyrolysis protocols. However, it is worthy of further study to find the optimal pyrolysis protocols for Ultem materials. Table 2 summarizes the gas separation performance of these polyimides-derived CMSMs. Principally, the selectivity of polyimides-derived CMSMs should be in the precursor order of Kapton (FFV = 0.11) > P84/Ultem   (FFV = 0.14) > Matrimid   (FFV = 0.17), consistent with their respective FFV values.

A few investigators have carried out intensive examination on the relationship between the chemical structure of polyimide precursors and the gas separation performance of their resultant CMSMs. Takeichi et al. studied the carbonization and graphitization of polyimides (PMDA-PDA, PMDA-ODA, and BPDA-PDA) by focusing on the effect of precursor's moiety structure on CMSMs (47, 48, 63, 64). Their polyimide films were prepared from two different precursors; namely, poly(amide acid) and poly(amide ester). The carbonization and graphitization of polymers were carried out at $900°C$ and $2800°C$, respectively. They found that the polyimide films prepared from poly(amide ester) show higher graphitization as compared to those from poly(amide acid) after heat-treatment at high temperatures. In the case of rigid-rod polyimide, the degree of orientation of graphitized films increases with the larger leaving groups, such as alcohols or aldehydes. Although their carbon membranes are too dense to be utilized in gas separation, some useful information about graphitization has been generated.

Korean researchers, Park et al. reported the effect of polyimides' microstructure on the gas permeation properties of CMSMs (52). A series of aromatic polyimides from dianhydride and diamines with a different number of methyl substituent groups was synthesized. The substitution of pendant groups into polymer backbone produces polyimides with higher T_g, fractional free volume (FFV) and d-spacing, and these values also increase with an increase in the number of methyl substituents. They reported that the final microstructure of resultant CMSMs is closely related to the chemical structure of polyimides. For example, an increase in d-space in polyimide precursors results in CMSMs with a larger d-space. In addition, the CMSMs carbonized from precursors with higher FFV are more permeable but less selective.

The above Korean researchers also introduced carboxylic acid groups into polyimide precursors and investigated their effects on CMSMs (65). The interaction of hydrogen bonds between the carboxylic acid pendant groups has led to the polyimide with relatively high chain packing and rigidity. As a consequence, these polyimides have high density and lower FFV. Contradictory to the previous finding, the CMSMs derived from

Table 2. Gas separation properties of CMSMs derived from commercially available polyimides

Carbon membrane	Membrane type	Test temp. (°C)	Test pressure (atm)	Permeability (barrier)				Selectivity			Ref.
				O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4	CO_2/N_2	
P84-CMSM	Self-support film	35	10	158	17.8	499	5.6	8.9	89	28	(68)
Matrimid-CMSM	Self-support film	35	10	227	30.3	611	10.0	7.5	61	20	(92)
Kapton-CMSM	Self-support film	35	1	34.8	3.04	128		11.5		42.2	(4)
Ultem-CMSM	Supported on macroporous carbon disks	25	1	~4	~0.5	~10	~0.4	7.4	25	15	(23)

All membranes were pyrolyzed at 800°C under vacuum but with different heating protocols.

these polyimides containing removable carboxylic acid groups are highly porous with large pore volume and less compact structures. The WAXD data confirmed that the resultant CMSMs have large interlayer space, while their gas permeability increases but their selectivity decreases with an increase in carboxylic acid content. Compared with the preceding two works, one may conclude that the thermal stability of polyimide plays a much more important role than the FFV and d-spacing of polyimide on gas permeation properties of CMSMs. This hypothesis has also been supported by Shao et al., who elucidated a much higher permeability and selectivity can be attained by CMSMs derived from 6FDA-durene than from Matrimid (56) at the same carbonization temperature. The former has the following advantages over the latter: (1) the ease release of CF_3 groups during the decomposition, (2) better carbon pore distribution and interpenetration caused by homogeneous CF_3 groups in 6FDA structure, and (3) less pore collapse at the high temperature process due to its high chain rigidity and high T_g.

Furthermore, the relationships between the structural properties of aromatic polyimides and their derived carbon membranes were also discussed by Xiao et al. (66). Unlike the other investigation that mainly focused on the FFV point of view, Xiao et al. explored the factors of chemical structure and physical properties of polyimides on the characteristics of the derived CMSMs through both experimental and simulation approaches. A series of aromatic polyimides were synthesized in their work in order to study how the thermal stability, microstructure and chain conformation of polyimides affecting the characteristics of CMSMs. These polyimides have been synthesized from diamine DAI (5,7,-diamino-1,1,4,6-tetramethylindan) and corresponding dianhydrides, i.e., 6FDA (2,2′-bis(3,4′-dicarboxyphenyl) hexafluoropropane dianhydride), BTDA (3,3′4,4′-benzophenone tetracarboxylic dianhydride), BPDA (3,3′4,4′-biphenyl tetracarboxylic dianhydride) and ODPA (3,3′4,4′-oxydiphthalic dianhydride). According to the experimental results, Xiao et al. concluded that, other than FFV, the thermal stability of precursors is also an important parameter to determine the microstructure of the resultant CMSMs, especially at a low pyrolysis temperature (i.e., 550°C). Generally, precursors with high FFV but less thermally stable will produce more permeable but less selective CMSMs. In addition, they discovered that the degree of graphitization of carbon membranes is somewhat manipulated by the molecules flatness and in-plane orientation of precursors. A "RIS" Metropolis Monte Carlo (RMMC) method was employed to calculate and quantify the flatness of polyimides molecules and their in-plane orientation along the film surface. The simulation results of chain properties are tabulated in Table 3. Correlation between the experimental and simulation data showed the CMSMs pyrolyzed from polyimides with good chain flatness and in-plane orientation at a high temperature (i.e., 800°C) exhibited high gas selectivity due to the formation of more graphitic-like structure during carbonization.

Table 3. The simulated results of chain properties for four polyimides

	BTDA-DAI	ODPA-DAI	BPDA-DAI	6FDA-DAI
Dihedral angle (°)	58.5	66.0	40.1	76.9
Mean squared end to end distance ($\mathring{A}^2$)	23,403	19,510	27,047	15,512
Molar stiffness function ($g^{0.25}cm^{1.5}/mol^{0.75}$)	236	205	260	183
Intrinsic viscosity (cm^3/g)	36.5	28.47	48.1	15.77

Last, researchers from Japan, Islam et al., had prepared flexible pyrolytic membranes by carbonizing the sulfonated polyimides at a relatively low temperature of 450°C under an inert nitrogen environment (67). The unique of their approach was that the low-temperature pyrolysis increases the gas permeability while sustaining the toughness of membranes. During low-temperature pyrolysis, the sulfonic acid groups ($-SO_3H$) decompose without substantial cleavage of polyimide backbone. Thus, their carbon membranes exhibit not only high flexibility but excellent separation properties. The microvoids formed by the decomposition of sulfonic acid groups provide large free volume, which contributes to high permeability. In addition, the rate of increase in gas permeability after pyrolysis is consistent with the increasing order of $-SO_3H$ content in the polyimide precursors. Furthermore, their pyrolytic membranes show high permeability and selectivity for the separation of C_3H_6/C_3H_8. Consistent with the previous studies, the authors concluded that the $-SO_3H$ content in the polyimide precursors, the relaxation of the polymer chains during the pyrolysis and the gas permeation level of the precursor membranes appear to be the important factors in controlling the gas permeability of partially pyrolytic membranes.

In summary, the above findings suggest that the physicochemical properties and chemical structure of polymer precursors are the crucial parameters for pyrolysis to tailor the microstructure and permeation properties of CMSMs. Various polyimides can be architectured and synthesized from different dianhydride and diamine monomers. Moreover, chemical modifications such as sulfonation, acidization, cross-linking, etc. are also the common methods used to further alter the structural properties of polyimides. In other words, polyimides precursors for carbon membranes can be designed and prepared in a variety of chemical structures with distinct physicochemical properties corresponding to a specific separation task. In general, it is important to consider FFV and d-space as the important criterions in choosing an appropriate polymer precursor for carbon membranes.

It is expected that polymer precursors with a smaller FFV and d-space will produce carbon membranes with a denser structure. On the contrary, a

polymer precursor with a larger FFV and d-space should be chosen if high permeability is required for the resultant carbon membranes. Moreover, the chain conformation of precursor, particularly molecules flatness, in-plane orientation, chain rigidity as well as the relaxation of polymer chains during carbonization also plays an important role in determining the pore evolution and microporosity of resultant carbon membranes. Besides that, there are some other decisive factors that could significantly govern the separation properties of carbon membranes, for instance, the thermal stability of precursor, size and ease release of substituent groups, steric properties of polymer, T_g, etc. With reference to the above criterions, engineering design of carbon membrane separation system requires careful identification of precursor materials based on structure-properties relationship.

Effect of Polymer Blends and Additive Mixtures

Rather than synthesizing new precursors to manipulate the microstructure of carbon membranes, modifications of polymeric precursor through polymer blending and incorporation of additives into the precursor matrix provide alternative approaches to customize the morphological and permeation properties of CMSMs. Four approaches have been developed as follows.

Mesoporous CMSMs Derived from Polymer Blends

The upper route in Figure 4 illustrates the concept of polymer blend carbonization. The presence of additives in the polymer matrix as well as the compatibility and miscibility of polymer blends can influence the precursors' degradation routes during the carbonization to a great extent. Decomposition of precursor materials determines the formation of pores, where thermally
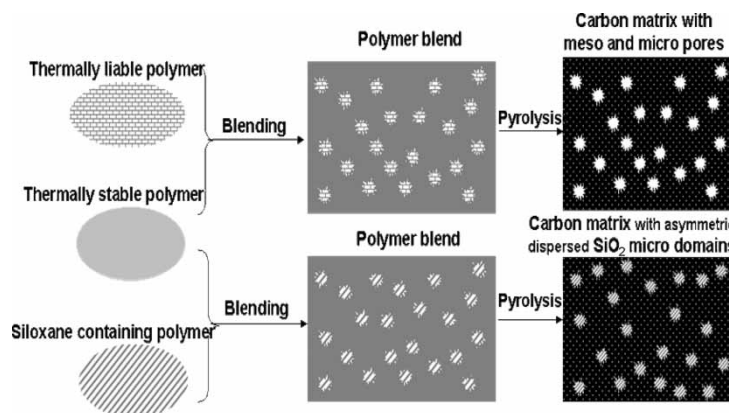

Figure 4. Carbonization of polymer blends.

labile polymer results in mesopores (2–5 nm), while the decomposition of thermally stable polymer creates micropores (<2 nm). Based on the differences of the thermal stabilities of polymers, polymer blending provides a way to alter the pore size distribution of CMSMs.

Ozaki et al. (71) were one of the pioneers describing a preparation method for the production of mesoporous carbon fibers by blending the phenolic resin with poly(vinyl butyral). A similar study has been carried out by Hatori et al. on a polyimide precursor, where mesoporous carbon membranes were prepared from carbonization of polyimide/poly(ethylene-glycol) blends (72). The high compatibility between the polyimide and poly(ethylene glycol) (PEG) were substantiated by XRD spectra. Unlike the microporous structure of CMSMs derived from neat polyimide polymer, blending of PEG with polyimide induced the formation of mesopores in addition to micropores. The mesopores were generated through the decomposition of PEG domains at around 400°C before the degradation of polyimide. Predictably, the mesoporous structure of CMSMs can be enhanced by increasing the PEG content in polyimide blends. Nevertheless, their experimental results demonstrated no definite correlation between the average molecular weight of PEG and mesopore size distribution. Furthermore, Kim et al. blended the polyimide with polyvinylpyrrolidone (PVP) to develop the porous structure of CMSMs (73, 74). Similar to PEG, PVP is well-known as one of the pore-forming agents in the polymeric membranes fabrication. From the TGA thermogram, the complete degradation of PVP occurred at 350–450°C before the decomposition of polyimide at the temperature range of 550–650°C. Therefore, the introduction of thermally labile PVP in blended polymeric precursors is expected to promote highly porous structure of CMSMs. Their WAXD results confirmed that the average d-spacing increased with PVP content. The CMSMs prepared in their study exhibited the Langmuir isotherm (type I) for nitrogen adsorption according to the IUPAC classification. This revealed that no meso- or macropores were formed during pyrolysis of precursors. Nevertheless, the increase of pore volume indicated the development of microporous structure in CMSMs with the addition of PVP in precursors. Consequently, the reduction of membranes resistance for gas transport and increment of diffusional pathway had improved the gas permeability.

For the same reason, the CMSMs derived from thermally unstable PVP blended polyimide precursors possessed lower selectivity as compared to CMSMs based on neat polyimides. Kim et al. also reported the higher molecular weight of PVP in the blended precursors led to microporous CMSMs with a larger pore volume. Accordingly, the introduction of high molecular weight PVP into polyimide precursors resulted in highly permeable but less selective CMSMs. The different conclusions on the effect of additives' molecular weight on mesopore size between Hatori et al. (72) and Kim et al. (73, 74) may possibly arise from different cast solution preparations, homogeneity and sizes of additives, and solution viscosity in the casting solution and the membranes.

Siloxane and Silica-Filled CMSMs

With reference to the effect of polymer blends, the introduction of additives in the precursor matrix may also have an impact on the porous structure formation in CMSMs through the disruption of carbon chain organization during pyrolysis. Thermal stable and liable polymer blending methods can be used to prepare carbon membranes designed with high gas permeability. However, the improvement of gas permeability is based on the sacrifice of gas selectivity. Moreover, the meso-pore structure will weaken the mechanical properties of carbon membranes. To overcome this difficulty, meso-pore structures can be replaced by other inorganic structures such as siloxane and silica, which not only have higher gas permeability but also certain mechanical strength, demonstrated as the lower route in Figure 4.

Park et al. had fabricated and characterized the carbon membranes containing silica through the pyrolysis of imide-siloxane copolymers (PSI) (75–79). In contrast to polymer blends, which make use of thermally unstable polymers to induce the formation of meso-porous structure in pyrolyzed membranes, the precursor preparation in this study involved two thermally stable polymeric materials, namely polyimide and poly(dimethyl siloxane) (PDMS). This two-phase copolymer composed of rigid and flexible building blocks founded by aromatic imide and siloxane moieties. As a result, the polymeric precursor can conserve the initial skeleton and structural characteristics of each domain after high-temperature treatment. Pyrolysis of imide-siloxane copolymers produced carbon membranes containing embedded silica in a continuous carbon matrix (C-SiO$_2$).

This has been verified by FTIR analysis, where a partial Si-O-Si network or silica phase was constructed in carbon membranes via pyrolysis of the organosiloxane phase in copolymers. Accordingly, the interplanar distances of membranes were affected by existence of organosiloxane domains in the polymer matrix, and the d-spacing values increased with increasing in siloxane content. Different from meso-pore CMSMs prepared from a thermally stable and liable polymer blend, the asymmetric structure of C-SiO$_2$ in the silica-filled CMSMs was disclosed by ESCA, FESEM, EDX, and TM-AFM spectra. Typically, the top surface of carbon membranes was rich with SiO$_2$, while the bottom surface was mainly the carbon-rich phase with well-dispersed SiO$_2$ in carbon bulk, as proposed in Figure 4. For the gas transport in the C-SiO$_2$ membrane, the carbon-lean phase originated from siloxane blocks offered the broad pathway for gas permeation, especially for small gas molecules. Concurrently, the carbon-rich phase transformed from aromatic imide blocks furnished the C-SiO$_2$ membranes with promising molecular sieving capability. As a result, the composite carbonaceous membranes displayed excellent separation selectivity with considerably high permeability. Similar to the polymer blends, the gas permeability increased but selectivity declined with an increase in siloxane moiety concentration.

On the other hand, Park et al. also synthesized two imide-siloxane copolymers with different morphologies, which are random and block at a constant siloxane volume fraction. The characteristics and permeation performance of the resultant composite membranes, denoted as r-C-SiO$_2$ and b-C-SiO$_2$ were evaluated. The microporous r-C-SiO$_2$ was comprised of small dispersed silica domains in carbon matrix, while the large silica domains were observed in the b-C-SiO$_2$. At identical pyrolysis temperatures, the average d-space of r-C-SiO$_2$ was also smaller than that of b-C-SiO$_2$, and the pore size distribution was narrower in the carbon membranes with random geometry than in the block geometry. Correspondingly, the higher gas permeability but lower selectivity was achieved by b-C-SiO$_2$ as compared to the r-C-SiO$_2$. At a constant volume fraction, larger siloxane domain (longer PDMS chain) within the PSI contributed to higher permeability but there was a slight reduction in selectivity for both precursor and its resultant pyrolytic membrane. Therefore, it is concluded that the microporous structure and gas permeation properties of C-SiO$_2$ were significantly influenced by the size and shape of siloxane moiety in the copolymers.

Metal-Filled CMSMs

Despite of silica, metals have also widely been used as the filler in carbon materials. However, the research on the gas separation using metal-filled CMSMs is not as in-depth as the preceding two types of filled CMSMs. The metal state in CMSMs and gas transport mechanism are still complicated and worthy of study.

The filled CMSM containing alkali metal ions was developed and prepared by Kim et al. based on the metal-substituted sulfonated polyimide as a precursor (80). The ion with a bigger radius was accountable for the increase in d-space of polyimide chains and subsequently increased the interplanar space of CMS membranes. As a result, the gas permeability of CMS membranes increased with increasing ionic radius of the substituted metal ion, whereas the gas selectivity decreased in the same order.

Kaburagi et al. developed carbon films through the pyrolysis of aromatic polyimide films containing transition metal (81, 82). In their works, several magnetic metal salts such as nickel nitrate, acetylacetonate iron (III) and cobalt chloride were first mixed with the polyamic acid in solutions followed by imidization. The changes of structure, texture and magnetic properties of composite polyimide films after carbonization were investigated. It was found that the nickel particles were formed in the carbon matrix via heat treatment above 400°C. The mean particle size increased with increasing heat temperature, and caused the change in magnetic property from superparamagnetic to ferreomagnetic. Fine particles of transition metals in polyimide revealed considerable catalytic effects on carbonization and graphitization. The fine iron particles with nano- and submicron sizes distributed

homogeneously in the carbonized films and promoted the extension and stacking of layers of matrix carbon.

Perhaps the first application of this type of carbon metal composite membranes for gas separation was reported by Barsema et al. (83). Their carbon molecular sieve membranes contained Ag-nanoclusters that showed a slightly improved selectivity on O_2/N_2 than non-Ag CMSMs. The increase in selectivity was attributed to a more selective gas transport channel between the Ag-nanoclusters and carbon matrix. Due to the stronger adsorption of O_2 on the Ag-nanoclusters, the permeation of O_2 in this channel was much faster than non-adsorbable N_2. They also reported that the gas separation performance of the metal-carbon composite films was partially determined by the metal particle size distribution, as smaller particle size contributing to larger surface area that generates more gas selective channels.

Moreover, to enhance the hydrogen separation selectivity, CMSMs doped with noble metals was prepared by Yoda et al. (84). The membranes were prepared through a new method; namely, supercritical impregnation. The impregnation of Pt- and Pd- nano-particles into polyimide films was achieved by dissolving organometellic compounds in supercritical CO_2 followed by thermal decomposition. After carbonization, the majority of metal particle size was less than 5 nm in diameter. The hydrogen selectivity of the resultant membranes was 17 times higher than that of non-doped CMSMs. Authors associated this increment to the inhibition of nitrogen mass transport by Pd particles.

Zeolite-Filled CMSMs

Tin et al. developed and investigated a carbon-zeolite mixed matrix composite membrane in which zeolites KY are a dispersed phase in a continuous carbon matrix (85). The composite carbonaceous membrane was easily fabricated through the pyrolysis of polymer-zeolite mixed matrix membrane. A homogeneous distribution of zeolites in carbon matrix and good carbon-sieve contact were acquired, as revealed by SEM pictures in Figure 5. The resultant heterogeneous membranes benefited from the advantages of both carbon membranes and zeolites by offering the impressive separation competence. As compared to the CMSMs derived from unfilled precursor membranes, the composite carbon membranes showed a remarkable improvement in selectivity with slight decline in permeability for the separation of CO_2/CH_4.

It is undoubtedly that blending of polymers and incorporation of additives are useful approaches to functionalize the precursor materials for carbon membrane fabrication. Polymer blends are basically used to control the microporosity and material cost for carbon membranes. First and foremost, the thermal stability, compatibility and miscibility of polymers are the main parameters that have to be taken into consideration when preparing a polymer
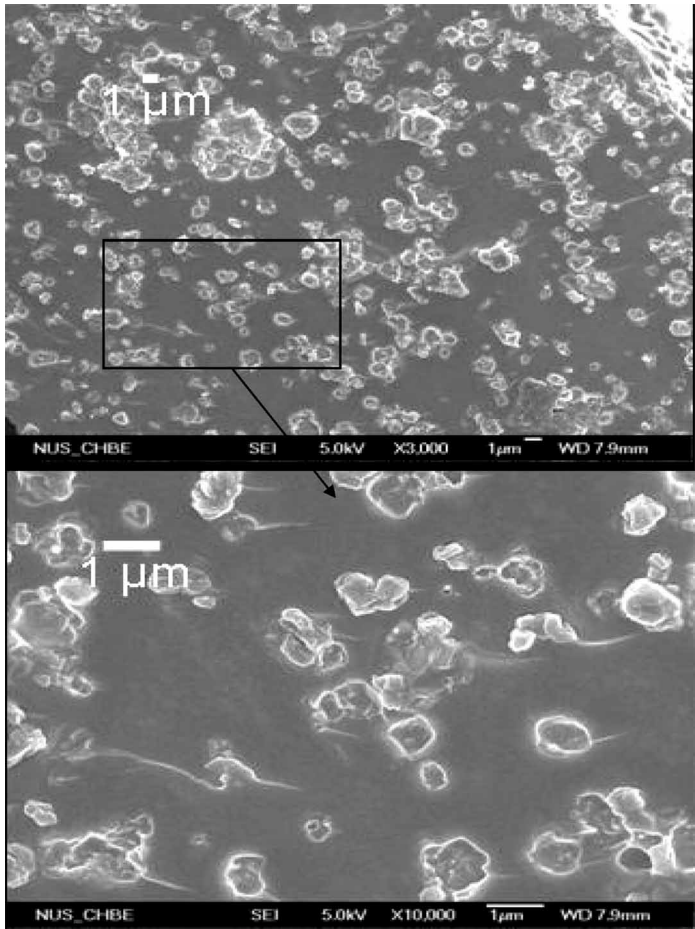
Figure 5. Scanning electron micrographs (cross-section) of a composite membrane containing zeolite KY in continuous carbon matrix at the (a) magnification of 3000, and (b) magnification of 10,000 (adapted from (85)).

blend for CMSMs, as the pore evolution is determined by the decomposition of precursor during carbonization. The common practice is to blend the thermosetting polymer (primary) with thermally unstable polymer (secondary) to promote the formation of macro- or mesopores in the carbon matrix. This is aimed to increase the diffusional path and hence the permeability of CMSMs. Nonetheless, the loss in selectivity will be encountered by the resultant carbon membranes. As a result, the selection of secondary polymer is critical, though the morphology and separation properties of CMSMs are dominated by the primary polymer. It is believed that blending of two or more thermally stable polymers with different degradation

paths and temperatures may have significant influence on the properties of pyrolyzed membranes. Subsequently, after selecting the suitable polymers, the most advantageous blending conditions, such as polymers composition and molecular weight of secondary polymer must be determined for the optimization of separation performance of the resultant carbon membranes.

Fabrication of composite carbon membranes with additives is also a complicated process. The choice of inserts is not arbitrary, but is based on the specific properties of a given material originating from its nature and structural factors. The common additives utilized for membranes separation technology are molecular sieves and adsorbents to gas molecules. Besides, separation efficiency of membranes can be also enhanced through other fillers, particularly metal particles attributable to the chemical bonding or complexation formed with certain gas molecules. The major challenges for the composite carbon membranes preparation are (1) prevent the agglomeration but ensure the uniform dispersing of insert particles in carbon matrix and (2) preparation of homogeneous composite CMSMs with good additive-carbon contact/adhesion. Park et al. have proposed an effectual method in fabricating the silica-containing carbon membranes through pyrolysis of copolymers (75–79). Unlike the ordinary approach by physical incorporation of inserts into the polymer matrix before carbonization, the method by Park et al. eliminates the possibility of inserts aggregation and induces good additive-carbon contact for resultant composite carbon membranes. Nevertheless, the embedded silica is mainly formed on the top surface of carbon membranes, rather than dispersing homogeneously in the carbon matrix. This is also one of the major problems encountered in preparing the composite CMSMs, where the insert particles tend to migrate onto the top surface of membranes during high-temperature treatment. Tin et al. have successfully overcome this problem by proper preparation of mixed matrix precursor membranes from a higher T_g polyimide and bigger zeolite particles with the thermal immobility process (85). In short, the selection of suitable polymer/filler pair, as well as preparation of homogeneous and defect-free mixed composite precursor membranes are the two major factors to produce high-performance composite carbon membranes.

Pretreatments of Polymeric Precursors and Their Effects on Resultant CMSMs

Many studies have reported that the optimization of pyrolysis conditions (pyrolysis temperature, heating rates, thermal soak time and pyrolysis environment) is essential to produce high performance CMSMs with tailored microstructures. Again, the selection and preparation of polymer precursor have also been proven as an important parameter in determining the separation performance of carbon membranes. Alternatively, the pore structures and properties of CMSMs can be finely adjusted to a specific

separation task through thermal and chemical treatments of precursor membranes. In other words, the pretreatment of polymeric precursors can be used to tailor the microstructure of derived CMSMs and improve the permeation properties or to solve several problems inherent to their structures for gas separation. This is due to that pretreatment alters the chain packing or chain segmental mobility of the precursor, thus may greatly affect the structural organization of membranes during the pyrolysis (86, 87). Basically, the purpose of pretreatment is to either pre-rearrange and/or stabilize the precursor structure before and during the high-temperature pyrolysis. It may also act to enhance the uniformity of pore formation in some cases (88). With the aid of specific pretreatment, high-performance carbon membranes with promising separation efficiency and stability can be produced. Current available pretreatment of precursors for CMSMs can be categorized into oxidation, physical and chemical treatments.

Oxidation Treatment

Oxidation or thermostabilization is the most popular and common technique used in pretreating polymeric precursors before pyrolysis. Many studies have proven that the oxidation plays an important role in formatting the carbon membrane performance. The pretreatment has shown its ability to prevent the melting or fusion of precursors, while avoiding excessive volatilization of element carbon in the subsequent carbonization step and maximizing the final carbon yield of carbon materials (18). The stabilization of precursors, especially the asymmetric structure of precursors, is very important to provide sufficient dimensional stability and prevent pores from collapsing during pyrolysis.

Depending on the precursor materials, the oxidation can be carried out in different ranges of temperatures, as well as thermal soak times under a variety of oxidative atmospheres. Pure oxygen (O_2), air and carbon dioxide (CO_2) are often employed for thermostabilization. One study involving the oxidation of polymer precursors has been carried out by Kusuki et al. (45), who thermally treated the polymeric hollow fiber precursors in atmospheric air at 400°C for 30 minutes before pyrolysis. It was ascertained that the oxidation equipped asymmetric precursor membranes with sufficient morphological stability for further high-temperature processing, or else softened the precursor during pyrolysis resulting in the CMSMs with poor separation performance.

Several groups of researchers such as Tanihara et al. (89), Okamoto et al. (6), as well as Yamamoto et al. (90) had also pre-oxidized their polyimide precursors before high-temperature carbonization. Once again, these studies showed that the thermostabilization process cross-linked the polymer chains and prepared a stable structure for withstanding the rigorousness of high temperature processing. Thus, oxidation is practical to enhance the selectivity without greatly reducing the permeation rate of carbon membranes, as

explored by Centeno and Fuertes (3). Consistently, the thermostabilization can also be applied on other polymeric precursors, for instance, polya-crylonitrile (36), phenol resin (91), or polyfurfuryl alhocol (28), as reported elsewhere (18).

Nonsolvent Treatment

Nonsolvent pretreatment of a polymer has been commonly used to induce polymer swelling and lead to higher free volumes. Thus, attempts were given to investigate whether swollen precursors can yield superior carbon membranes for separation through structural alteration. The importance of swelling effects on polyimide precursors, specifically the influence of non-solvent (methanol, ethanol, propanol, and butanol) pretreatment on the sepa-ration performance of carbon membranes was examined by Tin et al. (89, 94). It was found that the nonsolvent treatment weakened the polymer-polymer interaction, which was revealed by TGA data and reduced T_gs. In addition, the weak intermolecular interactions facilitated the structural reorganization of carbon chains during pyrolysis, and eventually caused the formation of smaller pores.

XRD data and PALS results confirmed the tighter chain packing and smaller pore size for the CMSMs fabricated with the nonsolvent pretreatment. For that reason, CMSMs derived from nonsolvent-treated precursors exhibited outstanding transport properties. Although the permeability of pretreated CMSMs was lower than untreated CMSMs, the selectivity was found to increase for CMSMs with nonsolvent pretreatment. From the trade-off curve in Figure 6, the best separation efficiency was obtained by carbon membranes pyrolyzed from ethanol-treated polymers. Conclusively, we have shown for the first time that the nonsolvent pretreatment is capable of inducing structural modification in the polymer precursors, thus facilitating the reorganization of carbon chains that leads to smaller selective micropores (CMSMs with higher ideal selectivity but lower permeability). In short, more selective carbon membranes were produced with tailored pore sizes and narrow pore size distribution after non-solvent pretreatment of precursor membranes.

Chemical Treatments

In view of the fact that pretreatment has significant effects in modifying and optimizing the separation properties of the resultant carbon mem-branes, another two modification approaches have been developed in our research studies. These modifications are based on chemical cross-linking and bromination on polyimides to enhance the separation capability of CMSMs (88, 92–95). Cross-linking pretreatment was performed on precursor membranes based on the concept about the space filling by cross-linking reagents may stabilize the structure of precursor to pyrolysis
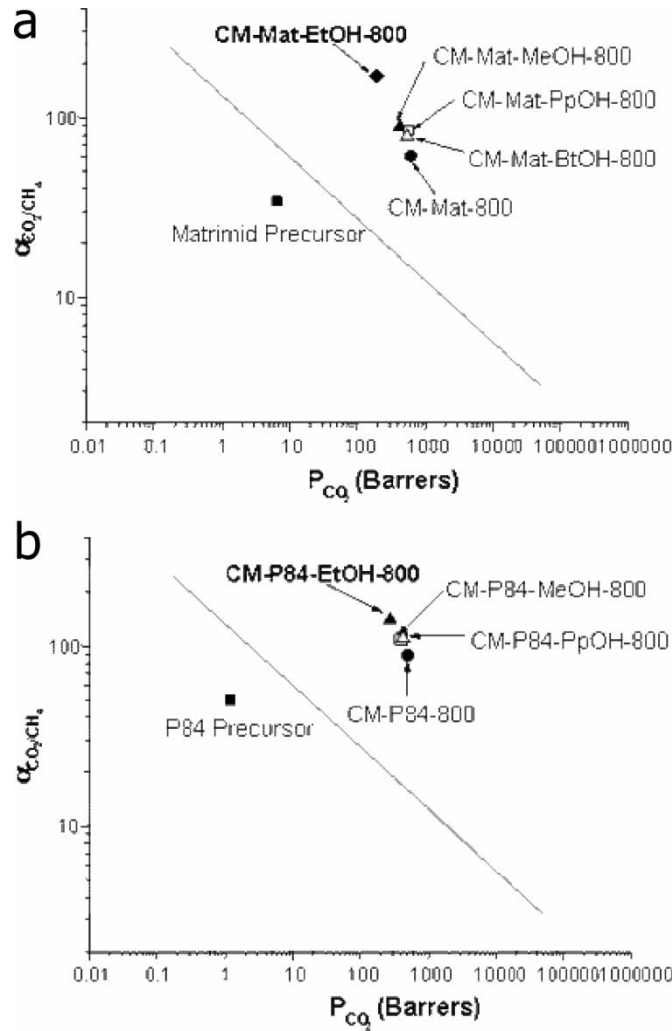
Figure 6. Separation properties of CO_2/CH_4 for (a) Matrimid-derived CMSMs and precursor, (b) P84-derived CMSMs and precursor with respect to the upper-bound curve (adapted from (88)).

temperatures. This is important to prevent the sudden collapse and softening of polymer chains and preserve the molecular configuration of membranes during the pyrolysis. A straightforward room-temperature cross-linking modification was performed on precursor membranes by immersing the polyimide films into cross-linking reagents for specific durations. CMSMs were then carbonized from cross-linked polyimide precursors at 800°C under vacuum environment (92, 93). The improved separation efficiency of CMSM with

reasonable high permeability was achieved at low degree of cross-linking, as compared to untreated CMSM. The enhanced separation performance of CMSMs at the low cross-linking density was presumably related to the swelling of polymer chains by methanol during cross-linking modification. Subsequently, the second extremely simple pretreatment method by using nonsolvent was developed.

Our last pretreatment on precursor membranes for CMSMs was accomplished by Xiao et al., who modified the properties of CMSMs by performing the bromination on polyimide precursor (95). This was aimed to understand the effect of thermal degradation of brominated polyimides during pyrolysis process. Intrinsically, bromination modification increased the molecules bulkiness but lowered the chain flexibility. It is substantiated that the micropore formation was affected considerably by the addition of these decomposable groups. Xiao et al. once again ascertained the important roles of thermal stability and FFV of polymers at low-temperature pyrolysis. Higher permeability with competitive selectivity was obtained for the CMSMs made from brominated Matrimid as compared to CMSMs from unmodified Matrimid. However, the gas permeability of the modified CMSMs was lower than that of unmodified CMSMs fabricated at elevated pyrolysis temperatures. RMMC simulation results revealed the bromination increased the linearity of polymer chains without changing the molecules flatness. Therefore, a higher degree of graphitization was acquired when brominated precursors were carbonized at high pyrolysis temperatures (800°C).

SUMMARY AND CONCLUSION

With development of advanced technologies, effectual membrane separation processes are required to conquer the immediate challenges and requirements in the gas separation. It is a formidable task to design a carbon membrane that can economically well fit the separation demands, especially in satisfying the separation productivity and efficiency. A researcher must take the following steps into consideration for the development of useful carbon membranes for gas separation: (1) precursor material selection, (2) precursor membrane preparation and modification, (3) pyrolysis of precursor membrane, (4) post-treatment of carbon membranes (optional), (5) membrane characterization and evaluation, and (6) carbon membrane module design. Figure 7 summarizes the strategies, and science and engineering principles of key players in this field and their technical considerations for the fabrication of promising carbon membranes.

The selection of precursor materials is clearly the most important factor in carbon membrane separation technology. Based on the literature, synthesis of polymers with different chemical structure, polymer blending, incorporation of additives in polymer matrix and pretreatment of precursor are available approaches to custom-design the precursor materials for
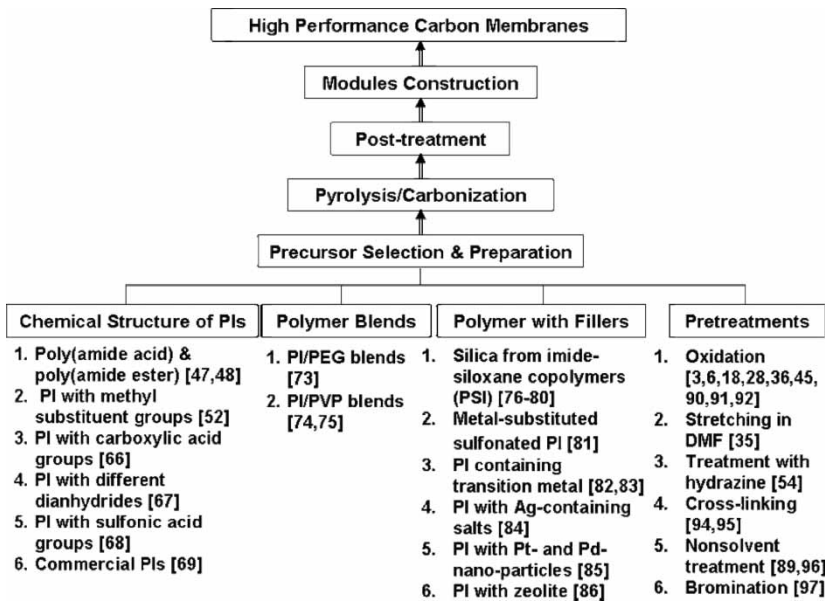
Figure 7. Overview of precursor selection and preparation for carbon membranes fabrication.

carbon membranes. Since the production cost involved for carbon membranes is extremely high, new polymer synthesis may not be economic, while modification of precursors, polymer blends and hybrid mixed matrix materials may be preferred in order to save the fabrication cost.

Besides being cost effective, polymer blending is one of the most simple and straightforward methods in tailoring the structure and properties of resultant materials. However, the phase separation of polymer blends will occur if two polymers are incompatible and immiscible. Thus, pairing of the suitable polymers for a blend is a major challenge to produce carbon membranes with desired properties for separation application. Lab-scale experiments have demonstrated that the selectivity of membranes can be easily enhanced through the incorporation of molecular sieves or adsorbents in the carbon matrix without a significant decline in permeability. Nevertheless, it is still not trivial to fabricate a defect-free composite carbon membrane with homogenous dispersion of additives in carbon matrix. In addition, most composite or mixed matrix membranes were prepared in the form of flat sheet membranes, which have much less economic value. The fabrication of carbon membranes in other configurations, especially the hollow fibers should receive more attention.

In contrast to other previously-mentioned approaches, pretreatments can be carried out on the precursor after formation of membranes, regardless of their configurations. The main drawback of this approach is the additional

chemicals and operation cost of pretreatment. However, the separation capability of carbon membranes can be remarkably improved by pretreatments, thus compensating for the additional pretreatment cost. Unlike chemical and physical treatments that involve the use of chemicals, the oxidation through heat treatment in air, O_2, N_2 or CO_2 is less complicated and problematic. This treatment is commonly programmed into the pyrolysis protocols as an additional carbonization step. Thus, thermostabilization is the most popular pretreatment technique to provide sufficient dimensional stability to membranes during pyrolysis.

Undoubtedly, the literature review clearly reveals that the structural properties and morphology of precursor materials impose significant effects in determining the microporous structure and separation properties of resultant CMSMs. Hence, matching of desirable carbon materials' performance characteristic with proper precursor materials is very imperative for the fabrication of high-performance carbon membranes.

ACKNOWLEDGMENTS

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