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To link to this article: http://dx.doi.org/10.1080/15422119.2011.555648

Published online: 02 May 2011.

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Precursor Selection and Process Conditions
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Carbon membranes prepared by pyrolysis/carbonization of polymeric precursors have been studied in the last few years as a promising candidate for gas separation process. As the aim of this paper, a review on polymer precursor selection and effect of pyrolysis conditions on carbon membrane characteristics and performances were discussed in detail. A number of different polymer precursors have been surveyed for their utility as materials in carbon membrane fabrication. The gas transport properties of various types of carbon membrane that produced by different researchers was summarized. Furthermore, the potential applications and future directions of carbon membrane in gas separation processes were also briefly identified.

KEYWORDS Precursor, stabilization, pyrolysis, carbon membrane, separation

INTRODUCTION

The development in the field of gas separation by membranes has seen the rapid increase since 1980s. It was accelerated by the development and
refinement of synthetic polymeric membranes, which eventually led to a commercial process on a large scale (1). As the technology advances and requirements for it become more demanding, new membrane materials are needed to satisfy separation productivity and efficiency. Carbon molecular sieve membrane is one of the new materials that have a potential to compete with available polymeric membrane. Carbon membrane is a variant to polymeric membrane. Basically, carbon membrane is constructed by heating a polymeric membrane beyond its decomposition temperature. Carbon membrane can give an excellent performance compared to polymeric membrane. A large volume of useful references on carbon membrane fabrication has been published in the literature. The first carbon molecular sieve membrane was successfully prepared by Koresh and Soffer in 1980 (2). However, extensive study on carbon membrane by other researchers was started in 1990s and the trend continues until today. The studies on carbon membrane are also documented in a number of patent works (3–8).

Ismail and David (9) wrote a review on the latest developments in the field of carbon membranes for gas separation. Later, Saufi and Ismail (10) extensively reviewed the fabrication of carbon membranes for gas separation. Those reviews concentrated only on the general fabrication aspects of carbon membranes including pre-treatment and post-treatment steps. The purpose of the current review is to provide an intensive overview regarding the development of carbon molecular sieve membranes during the last 30 years with a special emphasis on the pyrolysis conditions.

The review on the other inorganic membranes such as zeolite membranes also briefly discussed since it posses similar features to carbon membrane. To the authors’ knowledge, no review has so far been published on this subject. In addition, a clear future direction is given to further extend the research and development in the field of carbon membrane. The detailed discussions on polymer precursor selection, stabilization process, and pyrolysis process will be conducted. This paper also looks towards the process variables that exert great effects on the carbon membrane performances.

**INORGANIC MEMBRANE VERSUS POLYMERIC MEMBRANE**

Today, large-scale polymeric membrane systems are widely used in different separation processes and have dominated the membrane market in the world. It is mainly due to the availability of different types of low cost polymer materials that can be easily processed into a membrane that gives good separation and sufficient permeation flux. However, these membranes are not suitable to be applied in harsh environments, for example those prone to corrosion and high temperatures. As a result, inorganic membranes have rapidly received global attention in being considered as one of the potential candidates to replace available polymeric membranes. In membrane
processes, the permeability and selectivity are the most basic properties of a membrane that need to be considered.

It is well known that the membrane performance appears to be a trade-off between selectivity and permeability, i.e., a highly selective membrane tends to have a low permeability (11). Lu et al. (12) stated that the higher the selectivity and the more efficient the process, the lower the driving force (pressure ratio) required in achieving a given separation; thus resulting in lower operating costs for the separation system. The higher the permeability, the smaller the membrane area required; hence, the capital cost of the system is lowered. Therefore, some attempts have been made to prepare membranes that can surpass Robeson’s upper bound. Most of the membrane researchers have pointed out that the inorganic membranes have the potential to exceed such an upper bound. In this context, ultramicroporous (0.3–0.5 nm) membranes such as zeolite and carbon membranes have shown promise (13).

A large volume of information on zeolite membranes has been developed and can be easily obtained as compared to other types of inorganic membranes. Normally, zeolite membranes are prepared as a composite membrane with a thin layer of polycrystalline zeolite film coated onto a macroporous inorganic substrate. The substrate acts as a supporter whereas the zeolite film provides the selective layer that is responsible for the separation process. Zeolite is microporous crystalline silicates or aluminosilicates composed of \( \text{TO}_4 \) tetrahedra (T - Silicon or Aluminium atom) and oxygen atoms (14). There are several types of zeolites that are commonly categorized based on their framework structure. Figure 1 illustrates the structure of zeolite (15).

To date, most studies reported on gas separations with zeolite membranes have used MFI (ZSM-5) and LTA (Zeolite A) type zeolites. For example, Lavallo and coworkers (16) obtained a separation factor of about

![FIGURE 1 Structure of zeolite](a) cross section of a unit cell; (b) represents the small ultramicropores (0.42 nm) and larger micropores (1.14 nm) (15).
10 for CO₂/CH₄ separation using a high-silica MFI membrane. LTA zeolite membranes with H₂/N₂ selectivity of 7 were obtained by Guan’s group (17). This type of zeolites had pores in the range of 0.3–0.5 nm and was able to distinguish small molecules. Besides, some small pore zeolite, such as zeolite T (0.41 nm), DDR (0.36 × 0.44 nm) and SAPO-34 (0.38 nm) were a strong candidate for separation of CO₂/CH₄ because of the narrow windows that control molecular transport inside the material’s pores. These membranes possessed pores that were similar in size to CH₄ but larger than CO₂. As compared to polymeric membrane, DDR and SAPO-34 type zeolite membranes showed much higher CO₂ permeability and CO₂/CH₄ selectivity (18–22).

Theoretically, zeolite membrane has great advantages over other inorganic materials as an effective membrane layer due to its uniform pore structure at the molecular level. The first commercially available zeolite membrane was developed by Yoshio Morigami in 2001 (23) for ethanol dehydration using pervaporation process. However, the developments of zeolite membrane for gas separation application are still at the level of laboratory research. This is because it is very difficult to synthesize thin film zeolite membrane with fewer defects. As the membrane surface area increases, defects such as microcracks and intercrystalline boundary layer tend to form during the synthesis of zeolite membrane. In the gas separation process, a minor defect and thick skin layer in the membrane structure will dramatically destroy the separation performance.

Beyond the preparation challenges, there are also operational ones. The separation of bulky organics using zeolite membranes is complicated by the fact that these materials also adsorb on the surface of the pore and can actually block smaller molecules from permeating while being able to slip through themselves. Although the methods to prepare high quality zeolite membranes have been reported in the literature, the reproducibility of the zeolite membrane still cannot be achieved. This type of membrane also has poor mechanical stability and is much more expensive than the commercial polymer membranes with current state-of-the-art membrane manufacturing process.

The drawbacks posed by zeolite membranes have encouraged the researchers around the world to explore other types of inorganic membranes that can be applied in gas separation process, such as carbon membranes. Different from zeolite membranes, carbon membranes are usually prepared by pyrolysis/carbonization of polymeric precursor membrane at high temperature under vacuum or inert atmosphere. The similarities and differences between carbon membranes and zeolite membranes are represented in Table 1. After the heat treatment process, significant changes were observed in the resultant carbon membrane in terms of structure properties and separation mechanism. The differences between polymeric membranes and carbon membranes are also summarized in Table 1.
TABLE 1 Inorganic Membrane Versus Polymeric Membrane

<table>
<thead>
<tr>
<th>Separation mechanism</th>
<th>Polymeric membrane</th>
<th>Inorganic membrane</th>
<th>Carbon membrane</th>
<th>Zeolite membrane</th>
</tr>
</thead>
</table>
| Solution diffusion   | • Knudsen diffusion: >10Å  
                     | • Surface diffusion: <50Å  
                     | • Capillary condensation: >30Å  |
|                      | Similarity         | • Molecular sieving: <6Å  |
| Advantages            | • Low production  
                     | cost               | • Excellent chemical  
                     |                  | stability        |
|                      | • Surpass the trade-off  
                     |                  | between permeability  
                     |                  | and selectivity  |
|                      | Similarity         | • Create uniform pore  
                     |                  | structure at molecular  
                     |                  | level            |
|                      | • Excellent thermal  
                     | stability         | • Exhibit catalytic  
                     |      | property         |
|                      | • Can be used at aggressive  
                     | operation         |                  |
| Disadvantages         | • Poor thermal  
                     | resistance      | • Difficult to operate in  
                     |                  | bulky organic  
                     |                  | environment    |
|                      | • Poor chemical  
                     | resistance      | • High material cost |
|                      | • Arduous to  
                     | beach the trade-off  
                     | • Reproducibility in the  
                     |                  | synthesis method |
|                      |                  | between permeability  
                     | • Poor processability  
                     |                  | and selectivity  |
|                      |                  | and selectivity  
                     | • Difficult to synthesis  
                     |                  | membrane with a large  
                     |                  | surface area  |
|                      | Similarity        | • Brittle        |
|                      |                  | • High production  
                     |                  | cost              |

Generally, the change of the membrane separation mechanism is due to the change of the membrane structure. As shown in Figures 2(a) and 2(b), the pore wall of the membrane became rigid after converting to carbon membrane. Compared to polymeric membrane, carbon material can result in an amorphous structure with a wide pore size distribution and it is the same for carbon membrane. The pore mouth, ‘d’ or identified as an ultramicropore (<1 nm), allows molecular sieving of entrants to occur, while the larger micropores, ‘D’ (0.6–2 nm) may permit the diffusion of gas molecules to occur through the carbon material. Based on this pore structure, it is revealed that the best carbon materials not only have the ability to perform molecular sieving, but also allow a high flux of the entrants through the material (24).

In polymeric membrane, gases dissolve and diffuse through the membrane based on solution diffusion mechanism. The size (diffusivity) and
condensability (solubility) of the gas molecules would determine which component passes through the membrane faster. Three steps are involved in membrane permeation. They are: (i) the dissolution of the gas at the membrane interface; (ii) the diffusion of the gas through the membrane and (iii) the elution of the gas at the opposite interface (25). The molecules jump from free volume to free volume, while interacting with the polymer chains (26). In contrast, there are four possible mechanisms that would occur in carbon membranes and they are Knudsen diffusion, surface diffusion, capillary condensation and molecular sieving. These separation mechanisms would occur depending on the pore size of the membrane.

**STEPS INVOLVED IN CARBON MEMBRANE PREPARATION**

The concept of carbon membrane fabrication has attracted a great deal of attention among membrane researchers around the world in recent years. Basically, there are three stages involved in carbon membrane preparation, as shown in Figure 3.

A detailed review on precursor selection and process parameters that play an important role in carbon membrane preparation will be discussed in the following sections.

**PRECURSOR SELECTION**

In selecting polymeric precursor materials, not only thermal and chemical stability, but also a favorable combination of required permeability and selectivity and good mechanical properties of the carbon membrane
ultimately fabricated are sought for. Many authors have constructed carbon membranes from a wide range of polymeric precursors. The polymer precursor used should satisfy a number of criteria such as high aromatic carbon content, high glass transition temperature, $T_g$, chemically stable and provide superior separation properties (10, 27–29). Frequently used polymers are polyimides (27, 30–40), polyetherimide (41–45), and phenolic resin (13, 46–48). Other polymers such as polyfurfuryl alcohol (49, 50), polyphenylene oxide (51–54), poly(vinylidene chloride-co-vinyl chloride) (55), polycrylonitrile (56), sulfonated phenolic resin (57), phenol formaldehyde resin (58), polypyrrrolone (59), (trimethylsilyl)-substituted polyphenylene oxide (60), and poly(phthalazinone ether sulfone ketone) (61) have also been used quite successfully for preparing carbon membranes. Table 2 summarizes the polymer types that have been used as precursor for carbon membrane by various researchers.

Many studies reveal that the pyrolysis conditions impose strong effect on the gas permeation properties of carbon membranes. However, the pore dimensions and their distribution in the microstructure are not only significantly dependent upon the pyrolysis conditions, but are also affected by the selection of polymer precursors. As stated by Tin et al. (83), the chemical composition of polymer precursor is the crucial factors that determine the pore population created in the carbon matrix. Thus, this paper reviews several potential candidates of polymer precursors that have been extensively studied.

Polyimide

As reported in the literature, polymers like polyimide are excellent precursors to produce carbon membranes. Polyimide has been utilized extensively
TABLE 2 Carbon membrane prepared by previous researchers.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Configuration</th>
<th>Temperature (°C)</th>
<th>Heating rate (°C/min)</th>
<th>Thermal soak time (h)</th>
<th>Atmosphere</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>Hollow fiber</td>
<td>250</td>
<td>5</td>
<td>0.5</td>
<td>Air</td>
<td>(56)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500–800</td>
<td>3</td>
<td>0.5</td>
<td>N₂ (200 ml/min)</td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>Flat sheet</td>
<td>450–950</td>
<td>1</td>
<td>2</td>
<td>N₂/Ar</td>
<td>(62)</td>
</tr>
<tr>
<td>PEI</td>
<td>Supported on porous carbon disk</td>
<td>800</td>
<td>0.5</td>
<td>1</td>
<td>Vacuum (&lt; 0.01 mbar)</td>
<td>(31)</td>
</tr>
<tr>
<td>PEI</td>
<td>Supported on mesoporous tubular ceramic support</td>
<td>350</td>
<td>1</td>
<td>0.5</td>
<td>Ar (60 ml/min)</td>
<td>(42)</td>
</tr>
<tr>
<td>PEI</td>
<td>Supported on ceramic tubes</td>
<td>600</td>
<td>0.0167</td>
<td>0.5</td>
<td>Ar</td>
<td>(43)</td>
</tr>
<tr>
<td>PEI/PVP</td>
<td>Hollow fiber</td>
<td>400</td>
<td>3</td>
<td>1</td>
<td>Air (30 ml/min)</td>
<td>(44)</td>
</tr>
<tr>
<td>PEI</td>
<td>Supported alumina disk</td>
<td>200 (550,600,650)</td>
<td>1</td>
<td>12</td>
<td>Vacuum</td>
<td>(65)</td>
</tr>
<tr>
<td>PFA</td>
<td>Supported on macroporous graphite disk</td>
<td>90</td>
<td>3</td>
<td>3</td>
<td>Air</td>
<td>(64)</td>
</tr>
<tr>
<td>PFA</td>
<td>Supported on porous stainless steel support</td>
<td>100 (400–800)</td>
<td>5</td>
<td>1</td>
<td>Ar (200 ml/min)</td>
<td>(50)</td>
</tr>
<tr>
<td>PFR</td>
<td>Supported on porous ceramic sheet</td>
<td>800–950</td>
<td>2–3</td>
<td>N₂ (70–75 ml/min)</td>
<td>(58)</td>
<td></td>
</tr>
<tr>
<td>PFR</td>
<td>Supported on tube shaped support</td>
<td>150 (800–950)</td>
<td>0.5–1</td>
<td>Air (80–90 ml/min)</td>
<td>(65)</td>
<td></td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>Supported on porous carbon disks</td>
<td>850 (500–1000)</td>
<td>0.5</td>
<td>1</td>
<td>Air</td>
<td>(66)</td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>Supported on ceramic tubular</td>
<td>150 (700)</td>
<td>2</td>
<td></td>
<td>Vacuum</td>
<td>(47)</td>
</tr>
<tr>
<td>Sulfonated Phenolic resin</td>
<td>Supported on porous</td>
<td>110 (150)</td>
<td>5</td>
<td>10</td>
<td>Vacuum</td>
<td>(57)</td>
</tr>
<tr>
<td></td>
<td>α-alumina tubes</td>
<td>500 (500)</td>
<td>5</td>
<td>1.5</td>
<td>N₂ (100 ml/min)</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Support</td>
<td>Temperature</td>
<td>Pressure</td>
<td>Atmosphere</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
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<td>------------</td>
<td>------------------------</td>
<td></td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>Supported on ceramic tube</td>
<td>700–1000</td>
<td>10</td>
<td>1–8</td>
<td>Vacuum (&lt;1Pa) (48)</td>
<td></td>
</tr>
<tr>
<td>BPDA and aromatic diamines</td>
<td>Hollow fiber</td>
<td>400</td>
<td>0.5</td>
<td></td>
<td>N₂ (285ml/min) (30)</td>
<td></td>
</tr>
<tr>
<td>BPDA-pPDA</td>
<td>Supported on macroporous carbon disk</td>
<td>150</td>
<td>3</td>
<td>1</td>
<td>Air (41)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>1</td>
<td></td>
<td></td>
<td>Air (41)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>0.5</td>
<td></td>
<td></td>
<td>Vacuum</td>
<td></td>
</tr>
<tr>
<td>BPDA-pp’ODA</td>
<td>Supported on porous α-alumina tube</td>
<td>300</td>
<td>5</td>
<td>3</td>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>BPDA and aromatic</td>
<td>Hollow fiber</td>
<td>400</td>
<td>0.5</td>
<td></td>
<td>Air (33)</td>
<td></td>
</tr>
<tr>
<td>Diamines</td>
<td>Supported on macroporous carbon disk</td>
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<td>3</td>
<td>1</td>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>Matrimid</td>
<td>420</td>
<td>1</td>
<td></td>
<td></td>
<td>Vacuum</td>
<td></td>
</tr>
<tr>
<td>Polyimide (AP)</td>
<td>Hollow fiber</td>
<td>250</td>
<td>13.3</td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>535</td>
<td>3.85</td>
<td></td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>0.25</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.25</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>6FDA/BPDA-DAM</td>
<td>Flat sheet</td>
<td>550</td>
<td>2</td>
<td></td>
<td>Vacuum, Inert (67)</td>
<td></td>
</tr>
<tr>
<td>PI/PEG</td>
<td>Flat sheet</td>
<td>600</td>
<td>3</td>
<td>1</td>
<td>Ar (68)</td>
<td></td>
</tr>
<tr>
<td>6FDA/BPDA-DAM polyimide</td>
<td>Hollow fiber</td>
<td>A: 250</td>
<td>13.3</td>
<td></td>
<td>Vacuum (69)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>535</td>
<td>3.85</td>
<td></td>
<td></td>
<td>He</td>
<td></td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>0.25</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B: 250</td>
<td>13.3</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>785</td>
<td>3.57</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.25</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>P84 co-polyimide</td>
<td>Hollow fiber</td>
<td>150</td>
<td>50</td>
<td>0.25</td>
<td>(29)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>600–900</td>
<td>1</td>
<td></td>
<td>1</td>
<td>Vacuum (15)</td>
<td></td>
</tr>
<tr>
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<td>Flat sheet</td>
<td>550–800</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>LARC-TPI</td>
<td>Supported on porous α-alumina plate</td>
<td>A: 400</td>
<td>1</td>
<td>6</td>
<td>(70)</td>
<td></td>
</tr>
<tr>
<td>Polymide</td>
<td></td>
<td>B: 500</td>
<td>5</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C: 500</td>
<td>1</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precursor</td>
<td>Configuration</td>
<td>Temperature (°C)</td>
<td>Heating rate (°C/min)</td>
<td>Thermal soak time (h)</td>
<td>Atmosphere</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------------------------</td>
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<td>------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Matrimid</td>
<td>Flat sheet</td>
<td>250</td>
<td>13</td>
<td></td>
<td></td>
<td>(27)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>750</td>
<td>2.5</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>800</td>
<td>0.2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kapton</td>
<td>Supported on porous graphite disks</td>
<td>400</td>
<td>5</td>
<td>1</td>
<td></td>
<td>(37)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>550–1000</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kapton</td>
<td>Supported on porous graphite disks</td>
<td>400</td>
<td>5</td>
<td>1</td>
<td></td>
<td>(40)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600–800</td>
<td>0.5</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matrimid</td>
<td>Hollow fiber</td>
<td>400</td>
<td>2</td>
<td>0.5</td>
<td>N₂</td>
<td>(38)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>5</td>
<td>5</td>
<td>N₂ saturated with water CO₂</td>
<td></td>
</tr>
<tr>
<td>P84 co-polyimide</td>
<td>Hollow fiber</td>
<td>100</td>
<td>2</td>
<td>0.5</td>
<td>N₂</td>
<td>(39)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>5</td>
<td>0.083</td>
<td>N₂ (150ml/min)</td>
<td></td>
</tr>
<tr>
<td>Polypyrrole</td>
<td>Flat sheet</td>
<td>800</td>
<td>5–8</td>
<td></td>
<td>N₂</td>
<td>(59)</td>
</tr>
<tr>
<td>PPES</td>
<td>Flat sheet</td>
<td>440</td>
<td>2</td>
<td>0.5</td>
<td>N₂</td>
<td>(71)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650–950</td>
<td>1</td>
<td>1</td>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>PPESK</td>
<td>Flat sheet</td>
<td>460</td>
<td></td>
<td>0.5</td>
<td>Air (200ml/min)</td>
<td>(61)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650–950</td>
<td>1</td>
<td>1</td>
<td>Ar (200ml/min)</td>
<td></td>
</tr>
<tr>
<td>PPESK</td>
<td>Flat sheet</td>
<td>400–500</td>
<td>3</td>
<td>0.5</td>
<td>Air (150ml/min)</td>
<td>(72)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650–850</td>
<td>2</td>
<td>1</td>
<td>Ar (100ml/min)</td>
<td></td>
</tr>
<tr>
<td>PPESK</td>
<td>Flat sheet</td>
<td>460</td>
<td>3</td>
<td>0.5</td>
<td>Air (200ml/min)</td>
<td>(73)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650–950</td>
<td>1</td>
<td>1</td>
<td>Ar (200ml/min)</td>
<td></td>
</tr>
<tr>
<td>PVDC-PVC</td>
<td>Supported on porous carbon disk</td>
<td>150–200</td>
<td>1</td>
<td></td>
<td>Vacuum</td>
<td>(55)</td>
</tr>
<tr>
<td>PPO</td>
<td>Supported on tubular macroporous α-alumina ceramic support</td>
<td>700</td>
<td>5</td>
<td></td>
<td>Ar (200ml/min)</td>
<td>(51,54)</td>
</tr>
<tr>
<td>Material</td>
<td>Description</td>
<td>Temperature</td>
<td>Time</td>
<td>Gas</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------------------------------------</td>
<td>-------------</td>
<td>------</td>
<td>-----------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>PPO</td>
<td>Supported on tubular macroporous α-alumina ceramic support</td>
<td>500–800</td>
<td>5</td>
<td>1</td>
<td>Ar (200ml/min)</td>
<td>(52)</td>
</tr>
<tr>
<td>PPO</td>
<td>Supported on tubular macroporous α-alumina ceramic support</td>
<td>600</td>
<td>5</td>
<td>1</td>
<td>Ar (200ml/min)</td>
<td>(53)</td>
</tr>
<tr>
<td>PPO</td>
<td>Hollow fiber</td>
<td>280</td>
<td>0.75</td>
<td>Air</td>
<td>(60)</td>
<td></td>
</tr>
<tr>
<td>PAN/PEG</td>
<td>Hollow fiber</td>
<td>550–750</td>
<td>10</td>
<td>Vacuum</td>
<td>(74)</td>
<td></td>
</tr>
<tr>
<td>PAN/PVP</td>
<td>Flat sheet</td>
<td>270</td>
<td>0.5</td>
<td>Air</td>
<td>(75)</td>
<td></td>
</tr>
<tr>
<td>PI/PVP</td>
<td>Flat sheet</td>
<td>300</td>
<td>3</td>
<td>Ar (300ml/min)</td>
<td>(76)</td>
<td></td>
</tr>
<tr>
<td>PI/PVP</td>
<td>Flat sheet</td>
<td>550–700</td>
<td>3</td>
<td>1</td>
<td>Ar (300ml/min)</td>
<td>(77)</td>
</tr>
<tr>
<td>PFR/CMS</td>
<td>Supported on PFNR-based green membrane tube support</td>
<td>800</td>
<td>0.5</td>
<td>0.33–1</td>
<td>N2 (80ml/min)</td>
<td>(79)</td>
</tr>
<tr>
<td>PPO/PVP</td>
<td>Supported on tubular macroporous α-alumina ceramic support</td>
<td>500–800</td>
<td>5</td>
<td>1</td>
<td>Ar (200ml/min)</td>
<td>(78)</td>
</tr>
<tr>
<td>PFR/PEG</td>
<td>Supported on PFNR-based green membrane tube support</td>
<td>800</td>
<td>0.5</td>
<td>2</td>
<td>N2 (80ml/min)</td>
<td>(79)</td>
</tr>
<tr>
<td>PEI</td>
<td>Supported on porous alumina disk</td>
<td>150</td>
<td>1</td>
<td>1</td>
<td>Air (50ml/min)</td>
<td>(45)</td>
</tr>
<tr>
<td>PEI/PVP</td>
<td></td>
<td>500</td>
<td>0.5</td>
<td>1</td>
<td>Vacuum</td>
<td>(80)</td>
</tr>
<tr>
<td>PEI/MWCNTs</td>
<td>Flat sheet</td>
<td>250</td>
<td>10</td>
<td>2</td>
<td>Vacuum</td>
<td>(80)</td>
</tr>
<tr>
<td>SPAEK/Metal ions</td>
<td>Flat sheet</td>
<td>800</td>
<td>0.2</td>
<td>2</td>
<td>N2</td>
<td>(81)</td>
</tr>
<tr>
<td>PI-BTCOO Me/Cs CO3</td>
<td>Supported on porous alumina</td>
<td>200</td>
<td>5</td>
<td>2</td>
<td>N2</td>
<td>(81)</td>
</tr>
<tr>
<td>PI/MWCNTs</td>
<td>Supported on porous alumina disk</td>
<td>600</td>
<td>5</td>
<td>3</td>
<td>Vacuum</td>
<td>(82)</td>
</tr>
</tbody>
</table>
as carbon membrane precursor by numerous authors. However, some of these polymers are greatly limited from a practical point of view because they are expensive and not commercially available (10, 84). One of the synthesized polyimide is LARC-TPI. The LARC-TPI polymer was produced by imidization of polyamic acid through the dehydration in air under thermal treatment. The chemical structures of polyamic acid and LARC-TPI polyimide are shown in Figure 4. A partially carbonized membrane was prepared by pyrolyzing LARC-TPI polymer at 400–500°C. The resultant carbon membrane pyrolyzed at 500°C indicated high permeability for O2 of 1000–3000 Barrer and selectivity for O2/N2 of 3–6. This high permeability was contributed by the successive generation of flexible pores before the creation of graphite structure with rigid pores (70).

Kusuki et al. (30) fabricated asymmetric polyimide hollow fiber membranes by dry/wet spinning process for precursors of the asymmetric carbon hollow fiber membranes. Polyimides were prepared from 3,3’,4,4’-biphenyltetracarboxylic dianhydride (BPDA) and aromatic diamines. The solvent was p-chlorophenol. The precursors were treated under atmospheric air at 400°C before pyrolyzed at temperatures ranging from 600 to 1000°C under N2 environment. The asymmetric carbon membranes displayed high performance of gas permeability and selectivity for H2/CH4 separation. Supported polyimide-based carbon membranes were fabricated by Fuertes and Centeno (41) and Kusakabe et al. (32). Fuertes and Centeno (41) have successfully prepared a supported polyimide carbon membrane in only one casting step.
The gas permeation results indicated that the gas transport through the membrane occurs according to the molecular sieving mechanism. The selectivity measured at 25°C for the O₂/N₂, He/N₂, and CO₂/CH₄ systems were 5, 27 and 37, respectively. Kusakabe et al. (32) developed carbon membrane from BPDA-pp'ODA polyimide precursor supported on the surface of a porous alumina tube. This membrane showed high CO₂/N₂ selectivity of up to 40. It is concluded that, the permeation properties of the derived polyimide-based carbon membranes can be tailored by using different types of dianhydrides and diamines used for the synthesis.

Later, the researchers were more interested to use commercially available polyimides. It is because polyimide synthesis is time consuming and polymers are not easy to prepare. The common commercial polyimides used for producing carbon membrane are Kapton (DuPont) (34), Matrimid (15,27, 38, 69) and P84 co-polymer (39). The pyrolysis of Matrimid membrane up to 800°C has produced carbon membrane containing both ultramicropores (<7 Å) and larger micropores. The ultramicropores are believed to be mainly responsible for molecular sieving mechanism while the micropores provide negligible resistance to diffusion but provide high capacity sorption sites for penetrants. These carbon membranes are suitable for O₂/N₂, CO₂/CH₄, and C₃H₆/C₃H₈ separation (15).

Typically, carbon molecular sieve membranes are prepared from dense polymeric precursors that have already demonstrated good intrinsic gas separation properties. The rationale behind this approach is that the occurrence of any kind of initial porosity will deteriorate the final carbon membrane performance. However, carbon molecular sieve membranes from porous precursor were successfully prepared by Barsema et al. (29) using P84-polyimide. It was found that the pore diameter increased with increasing pyrolysis temperature up to 800°C, but decreased as the temperature was further increased to 900°C. According to these results, it can be concluded that it is not necessary to start with a gas selective precursor to produce selective carbon molecular sieve membrane for gas separation.

Different precursors require different process conditions and as a result, carbon membranes produced from different precursors have different properties, as proved by Fuertes and coworkers (34), Vu and Koros (69) and Favvas et al. (38). The permeability and selectivity data of Matrimid and Kapton derived carbon membranes indicate that the resulting carbon membranes possess molecular sieve properties and that they are suitable for the separation of permanent gases of industrial interest such as O₂/N₂, CO₂/CH₄, and CO₂/N₂. High permeability carbon membranes were obtained by using Kapton as precursor. Meanwhile, the Matrimid-based carbon membranes showed low permeability but higher selectivity. The selectivity of CO₂/CH₄, CO₂/N₂, and O₂/N₂ for a Matrimid derived carbon membrane was 33, 15, and 6, respectively (34).
Based on literature, it is believed that Matrimid-based carbon membranes are more selective compared to Kapton and P84-polyimide-based carbon membranes. It was evidenced by the articles published by Vu and Koros (69) and Favvas and coworkers (38). Vu and Koros (69) have compared the performance of carbon hollow fiber membranes derived from 6FDA/BPDA-DAM and Matrimid by pyrolysis using identical protocol. While, Favvas and coworkers (38) prepared carbon hollow fiber membranes from Matrimid and P84 co-polyimide (BTDA-TDI/MDI) precursor by pyrolysis up to 900°C.

The highest selectivity obtained for the P84 co-polyimide carbon membrane was 843, 12, 51, 2, 40 and 17 for $\text{H}_2/\text{CH}_4$, $\text{O}_2/\text{N}_2$, $\text{CO}_2/\text{CH}_4$, $\text{N}_2/\text{CH}_4$, $\text{CO}_2/\text{N}_2$ and $\text{H}_2/\text{CO}_2$ respectively. The selectivities of $\text{CO}_2/\text{CH}_4$ and $\text{CO}_2/\text{N}_2$ were 20 times higher than precursor membrane. Meanwhile, Matrimid carbon membrane exhibited $\text{H}_2/\text{CH}_4$ and $\text{H}_2/\text{CO}_2$ selectivity of 137 and 38, respectively. Other studies involving the use of polyimide precursor for carbon membrane synthesis were also reported by Tanihara et al. (33), Ghosal and Koros (35) and Tin et al. (83).

Polyetherimide

Polyetherimide (PEI) is one of the newest generic groups of engineering plastics and has a number of advantages as membrane materials. Studies on the PEI dense membranes have shown that, it exhibits good chemical and thermal stability as well as impressive separation factors. As polymeric membrane, PEI exhibits much higher selectivity compared to polysulfone and polyethersulfone (85). Although PEI polymer has lower gas permeability, its higher intrinsic selectivity for $\text{He}/\text{N}_2$, $\text{CO}_2/\text{N}_2$ and $\text{O}_2/\text{N}_2$ makes this polymer an attractive membrane material (86). PEI is considered as an advanced polymer which has both ether links and imide groups in its polymer chain. The aromatic imide units provide stiffness and heat resistance, while the swivel groups such as $-\text{O}$ and $-\text{C} (\text{CH}_3)_2$ form flexible macromolecular chains that allow for good process ability. The general structural formula of PEI is shown in Figure 5.

![Figure 5: Structural formula of PEI (42).](image)
Several research groups have recently studied the morphology and separation performance of carbon membrane using PEI as a precursor. Fuertes and Centeno (41), for example, used PEI polymer as a starting material for fabricating supported carbon membrane for O₂/N₂, N₂/He, and CO₂/CH₄ separation. The permselectivity of the carbon membrane for the O₂/N₂ system was 7 at 25°C. This membrane was successfully prepared by only one casting step. It is an important improvement with respect to the multicoating methods described in the literature for the preparation of defect-free supported carbon membrane. In 1999, Sedigh et al. (42) prepared carbon membrane by carbonization of PEI-coated mesoporous tubular supports at 600°C under Ar atmosphere. These membranes showed higher permeance and better selectivity than other supported carbon membrane reported in the literature for the CO₂/CH₄ and H₂/CH₄ binary mixtures as well as for the CO₂/H₂/CH₄ ternary mixture.

Selectivity as high as 145 for the CO₂/CH₄ equimolar binary and 155 for the CO₂/H₂/CH₄ ternary mixture were obtained. A year later, Sedigh et al. (43) investigated the effect of the coating/pyrolysis cycle on the substrate in order to find out where the selective carbon film is created and how it modifies the underlying support structure. Based on literature review, the quite promising performance of the supported PEI-based carbon membranes had successfully prepared. However, the preparation of carbon membrane from PEI in other configuration such as hollow fiber also necessary, because it exhibits better features compared to other types of configurations.

Polyacrylonitrile (PAN)

Polyacrylonitrile (PAN) polymers have been utilized in the area of carbon fiber production and conquer nearly 90% of all worldwide sales of carbon fibers. This material also has been known as the most promising precursor for the preparation of high performance carbon fiber (87). In carbon membranes field, the utilization of PAN as precursor to form carbon membrane started in early 1990s when Schindler and Maier (6) and Yoneyama and Nishihiro (88) prepared porous carbon membranes. Later, the use of PAN precursor was expanded by blending it with other polymers in order to alter the final pore size distribution of the carbon membrane and also by coating the PAN carbon membrane with zeolites to create composite membranes (74, 89). However, the detail of the separation performance offered by PAN based carbon membrane was not reported in those studies.

Since then, there was not much research involving the use of PAN as a precursor for carbon membrane conducted, until late 2003, when David and Ismail (56) prepared their PAN-based carbon hollow fiber membrane. These permeation data represent the first reported data for PAN as a precursor.
in literature. A low selectivity of the PAN carbon membrane was obtained and it was due to the lower selectivity of the initial PAN precursor and the presence of defects in the membrane surface, which diminished the ability of membrane to display molecular sieving characteristics. Recently, PAN-derived carbon membranes were extensively prepared and characterized by Song and coworkers (62). The carbon membranes were fabricated by carbonizing the PAN precursor membranes in vacuum and Ar atmosphere at different temperatures. The influence of pyrolysis atmosphere on the structure changes of PAN carbon membranes was studied by Fourier transform infrared spectroscopy, Raman and X-ray diffraction. Analytical results revealed that vacuum atmosphere could produce PAN carbon membranes with a higher degree of order than those in Ar atmosphere, although the structures of PAN carbon membranes prepared in these two atmospheres are both amorphous.

Phenolic Resin

Phenolic resin is one of the inexpensive polymers used as carbon membrane precursors. Centeno et al. (48) have successfully prepared carbon membrane by coating a phenolic resin on a macroporous carbon disk support in only one casting step. The optimum pyrolysis temperature was 700°C, at which the highest permeance was achieved. The resulting carbon membranes also exhibited excellent selectivities for the separation of $\text{O}_2/\text{N}_2$ (10), $\text{CO}_2/\text{CH}_4$ (160), and $\text{CO}_2/\text{N}_2$ (45). They concluded that, phenolic resin presents suitable features to be applied as carbon membranes precursors. Later, they developed carbon membranes by simple pyrolysis of a phenolic resin film deposited on a ceramic tubular support. The effect of variables involved in pyrolysis processing on the membrane performance was studied (13, 55, 66).

Carbon membrane based on phenolic resin was further investigated by Fuertes and Menendez (47) for the separation of hydrocarbon gas mixtures such as alkenes/alkanes and n-butane/iso-butane. The range of selectivity obtained for the ethylene/ethane, propylene/propane, and n-butane/iso-butane systems are 2–11, 10–50, and 10–40, respectively. Furthermore, Zhou et al. (57) have used phenolic resin as starting material to prepare carbon membrane by modifying it into sulfonated phenolic resin.

Sulfonated phenolic resin was synthesized by slowly adding p-phenolsulfonic acid into 37% formaldehyde solution, which was kept in ice water bath. The molar ratio of p-phenolsulfonic acid to formaldehyde was 1/0.60 to 1/0.66. The resulting carbon membrane displayed a high $\text{O}_2$ permeability (30 GPU) and $\text{O}_2/\text{N}_2$ selectivity (12) at 35°C. Nevertheless, in recent years these polymers are not getting a great attention from membrane researchers, although exhibit low material cost due to strong competition
with other polymers that have the same potential to be applied in carbon membrane preparation for gas separation application.

Polyfurfuryl Alcohol (PFA)

The characteristics of PFA that make this polymer have a potential to prepare carbon membrane are chemically stable, non-graphitizable structure of an amorphous polymer, simple molecular structure and formation mechanism and a narrow pore size distribution \(^{(10)}\). PFA has been extensively used as a precursor during the preparation of carbon molecular sieve membrane by Chen and Yang \(^{(64)}\). Defect free carbon membrane supported on a macroporous substrate was formed by coating a layer of PFA followed by controlled pyrolysis at 500°C under N\(_2\) atmosphere. The coating-pyrolysis procedure was repeated 5 times until carbon membrane layer of 15 \(\mu\)m was formed. The steady-state diffusion fluxes of single-component and binary mixtures of CH\(_4\)/C\(_2\)H\(_8\) through the carbon membrane were measured.

PFA also has been used as a precursor to prepare nanoporous carbon membrane. The selectivity for O\(_2\)/N\(_2\) separation of up to 4 was achieved for the membrane pyrolyzed at 600°C under He atmosphere. Then, the improvement of the coating technique was made to distribute the polymer onto the support uniformly. As a result, the reproducible nanoporous carbon membrane was successfully prepared, which improved O\(_2\)/N\(_2\) selectivity to a range of 2–30 and provided large separation factors for H\(_2\)/CH\(_4\), CO\(_2\)/CH\(_4\), N\(_2\)O/N\(_2\) and H\(_2\)/CO\(_2\) of 600, 45, 17 and 14, respectively \(^{(90–94)}\). Since PFA is in liquid form at room temperature, it only can be used for preparing supported membrane \(^{(64)}\). This limitation have make this polymer were rarely found in the literature.

Polyphenylene Oxide (PPO)

Among alternative polymeric precursors, poly (2, 6-dimethyl-1, 4-pyphenylene oxide) (PPO), having the glass transition temperature of 213°C, is considered to be one of the promising polymers for carbon membrane fabrication. Until now, the preparation of carbon membranes derived from PPO polymer and their permeation results have rarely reported. PPO has a linear structure assigned to the rotational motion of its phenyl ring, giving excellent mechanical properties. It is known that the PPO polymeric membranes have reasonably high gas permeability among aromatic polymeric membranes due to the presence of ether linkages and the absence of polar groups. Moreover, the methyl groups attached on both sides of phenyl ring hinder the free rotation of the phenyl ring resulting in relatively high permselectivity of PPO membranes. Figure 6 shows the molecular structure of PPO \(^{(54)}\).
Recently, Yoshimune et al. (60) have prepared carbon molecular sieve membrane derived from trimethylsilyl substituted PPO (TMSPPO). The PPO precursor was modified by introducing a trimethylsilyl (TMS) substituent and its effect on the gas transport property of the resulting carbon membrane was examined. From the microstructure analysis of the TMSPPO carbon membranes, it is believed that the TMS groups improve gas diffusivity by increasing the micropore volume. The molar content of the TMS group in the polymeric precursor also plays an important role on the $O_2$ permeability and $O_2/N_2$ selectivity. The $O_2$ permeability increased and the $O_2/N_2$ selectivity slightly decreased with an increase in the molar content of the TMS group, thereby suggesting that the TMS group has the potential to improve the performance of the PPO carbon membrane.

Poly(vinylidene chloride) (PVDC)

Poly (vinylidene chloride) (PVDC) was among the first synthetic polymers to be commercialized. This material is commercialized under trademark Saran. This material has been extensively investigated as precursor of carbon material 40 years ago. Lamond et al. (95) observed that carbons produced from pyrolysis of Saran up to 1000$^\circ$C resulted in carbons with 6 Å molecular sieve properties. In 1981, Kitagawa and Yuki (96) documented the preparation of carbon pellets by heat treatment of Saran waste, which exhibited molecular sieve properties similar to zeolite 5A. Centeno and Fuertes (55) prepared composite carbon membrane from PVDC supported over a macroporous carbon substrate.

In this study, the PVDC is produced as a copolymer with polyvinyl chloride (PVC) to improve the processability or solubility of this material. An almost defect-free carbon membrane was obtained in only one casting step. Single gas permeation experiments with pure gases of different molecular sizes ($He$, $CO_2$, $O_2$, $N_2$ and $CH_4$) have been performed. The best permeation
properties was achieved for membrane pyrolyzed at a temperature of 700°C and the selectivity up to 14 was obtained for O₂/N₂ separation.

Phenol Formaldehyde Resin (PFR)
Phenol formaldehyde resin (PFR), is a linear-chain condensation product, which is favored to prepare a nonporous dense layer. This resin has plastic property and melts when heated and the pinholes in dense layer are eliminated effectively. However, such property also results in deforming the support and the membrane cannot retain its shape during pyrolysis. As a result, the carbon membrane with low selectivity was obtained. To improve the selectivity, hexamine was added in resin. Thus resin became thermosetting resin during heat-treatment and the coating-pyrolysis cycle only needed one time. The resultant carbon membrane has shown a good selectivity for H₂/N₂ and H₂/CH₄ with H₂ permeance of $4 \times 10^{-6}$ cm$^3$ cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$. The membrane selectivity of H₂/N₂, H₂/CH₄, and O₂/N₂ was 24–40, 23–45, and 2–3, respectively (65). Shusen et al. (58) have successfully prepared an asymmetric carbon molecular sieve membrane by pyrolysis of a PFR. The membranes showed high permeability and selectivity. The selectivity of O₂/N₂ and H₂/N₂ was 11 and 24, respectively. To date, the high performance carbon membranes prepared from PFR are still rarely discussed and reported in international journals.

Polypyrrolone
Polypyrrolone is a step-ladder polymer with high thermal and chemical stability, and have a potential to be used as carbon membrane precursor. Because of the rigidity of the main chain of polypyrrolone, intersegmental packing and segmental mobility should be inhibited, providing a precursor for a carbon membrane with higher separation performance than polyimides. Figure 7 shows the molecular structure of polypyrrolone (59).

Carbon molecular sieve membranes based on polypyrrolone have been developed by Kita et al. (59) in 1997. Polypyrrolone was prepared by two step synthesis, i.e., preparation of poly (amidoamic acid) first, followed by thermal cyclodehydration of intermediate poly (amino imide). Then,
polypyrrolone membranes were heated up to 800°C. This polymer exhibited excellent stability up to 500°C, without weight loss from the membrane. The results reveal that an introduction of a ladder structure in the backbone chain of polyimide enhanced the gas permeability and maintained the selectivity of gases, owing to simultaneous inhibition of chain packing and intramolecular motion. The permeability of polypyrrolone membranes pyrolyzed at 500–700°C was enhanced by two orders magnitude compared with the precursor.

Poly(phthalazinone ether sulfone ketone) (PPESK)

Poly(phthalazinone ether sulfone ketone) PPESK is one of the synthetic polymers that possess high glass transition temperatures. The detailed synthesis procedure of PPESK was described elsewhere (97). Zhang and coworkers (61) had successfully prepared carbon membrane based on PPESK with well-developed microporosity after heat treatment. It was observed that two kinds of pores (ultramicropore centering at 0.56 nm and supermicropore centering at 0.77 nm) was created in the carbon structure and high gas separation performance was achieved. On the other hand, Liu’s group (72) reported that PPESK based carbon membrane of high H₂, CO₂, and O₂ permeability (1016, 710, 188 Barrer, respectively, with 1 Barrer being the gas permeability defined as 850 gas cm⁻³ per membrane cm over square cm per day and per gas pressure in bar) were obtained after pyrolysis at 650°C.

Meanwhile, the high selectivities for H₂/N₂ (129), CO₂/N₂ (93), O₂/N₂ (22) and O₂/N₂ mixture (24) were achieved by PPESK-carbon membrane pyrolyzed at 850°C. Recently, it was found that the microstructure and gas permeation of PPESK membranes and their carbon membranes could be improved by manipulating sulfone over ketone molar ratio (S/K). The performance of the carbon membrane derived from three different kinds of copolymer PPESK of ratio 20/80, 50/50, and 80/20 were studied. The PPESK-carbon membranes with the S/K ratio of 50/50 showed the best selectivity compared to those with the S/K ratio of 20/80 and 80/20. It is due to the dense and regular microstructure of the membranes (73). The study on the PPESK-based carbon membrane is still in early stage and extensive studies are required in near future, since it gives an excellent selectivity in various types of gas pairs.

Polymer Blends

Besides using pure polymer as precursors, the polymer blends with other polymers and inorganic materials also have attracted many researchers in production of carbon membranes. An early work regarding the use of
polymer blend as a carbon material precursor was disclosed by Ozaki and coworkers (98). In recent years, several carbon membranes fabricated from polymer blends have been reported such as by blending PPO/PVP (78), PEI/PVP (44, 45), PAN/PEG (74), PAN/PVP (74), PI/PEG (68), PI/PVP (75, 76), PFNR/PEG (79) and PBI/PI (99). Kim et al. (75) fabricated carbon membrane from PI/PVP blends by controlled pyrolysis. Experimental results show that the gas permeability through the carbon membranes was enhanced by the introduction of thermally labile polymer, which was PVP and decreased as the final pyrolysis temperature was increased. The high O\textsubscript{2} permeability of 630 Barrer and O\textsubscript{2}/N\textsubscript{2} selectivity of 10 was obtained. It is believed that the introduction of the thermally labile polymer leads to control of the pore structure of carbon membrane.

The gas permeability of carbon membrane increased with increasing molecular weight of thermally labile polymer. This is because resistance to gas permeation through carbon membrane was reduced by the formation of larger accessible pores obtained from thermally labile polymer. Meanwhile, the pathways of diffusion for the transport of gas molecules through the carbon membrane increased (76, 78, 89). An intensive study on carbon membrane preparation from PPO and PPO/PVP precursor has been done by Lee’s group (51–54, 78). Coutinho et al. (44) fabricated carbon membrane by the pyrolysis of PEI/PVP hollow fiber membranes and studied the influence of process variables on the final membrane morphology using a statistical experimental design. Rao et al. (45) prepared PEI/PVP-based carbon membranes by spin coating technique using porous alumina disk as support.

Furthermore, the incorporation of solid particles such as zeolite, silica, and carbon nanotube within membranes has also been utilized in carbon membrane fabrication. Rao et al. (45), for example, have modified PEI precursor to produce carbon membrane by blending with multi-wall carbon nanotubes (MWCNTs). The best performance obtained by PEI/MWCNTs carbon membrane was CO\textsubscript{2} permeability of 1463 Barrer and O\textsubscript{2}/N\textsubscript{2} permselectivity of 24. It was found that the gas diffusivity improved by the addition of inorganic particles even when they were not well dispersed in the carbon membrane (24, 77, 100–102). The MWCNTs offered a favorable effect in increasing gas permeability by decreasing the gas diffusion resistance. By the incorporation of MWCNTs the permeability of CO\textsubscript{2}, N\textsubscript{2} and O\textsubscript{2} were all increased and the ideal selectivity of CO\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/N\textsubscript{2} increased 2 and 1.5 times, respectively, for carbon membranes derived from PI/MWCNTs (82).

Zhang et al. (103) have emphasized that the composite carbon membranes from PPESK loaded with PVP and zeolite were good candidates for membranes for gas separation. They studied the effect of incorporating zeolite and PVP in PPESK-based carbon membrane. These two additives can drastically improve the gas permeability of H\textsubscript{2}, CO\textsubscript{2} and O\textsubscript{2} by 7–20 times along with the reduction in the selectivity of H\textsubscript{2}/N\textsubscript{2}, CO\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/N\textsubscript{2} by
35–90% for resulting composite carbon membrane. The O₂ and CO₂ permeability through carbon membrane based on poly (imide siloxane) was increased more than 3 times by the addition of alumina (104).

In addition to thermal labile polymer, carbon nanotube and zeolite, there are attempts to add metal ions into polymeric precursors before carbonization. Xiao et al. (80) reported the fabrication of carbonized sulfonated poly (aryl ether ketone) (SPAEK) membranes with different counter-ions (H⁺, Na⁺ and Ag⁺) as additives. Comparing the permeability of carbon membranes with their respective precursor, only SPAEK/Ag⁺-based carbon membrane shows enhanced gas permeability upon carbonization at 800°C. The higher ideal gas selectivity of CO₂/CH₄ and H₂/N₂ gas pairs were also presented for SPAEK/Ag⁺ than SPAEK/H and SPAEK/Na carbon membranes. Kai et al. (81) discovered that the problem of separation performance decline under humid conditions was improved by incorporation of Cesium (Cs) in polymeric precursor solution. The separation performance was evaluated using a CO₂/N₂ gas mixture with controlled relative humidity at 40 °C and at atmospheric pressure. The results showed that the carbon membranes without Cs had a lower CO₂ permeability and CO₂/N₂ separation factor under humid conditions than it did under dry conditions. On the other hand, Cs-incorporated carbon membranes had a higher CO₂ permeability and separation factor under wet conditions.

In summary, among polymeric precursors mentioned above, the aromatic polyimide-type polymer appears to be one of the most promising materials to yield carbon membranes with superior separation properties. Although a substantial amount of article has been published on the gas separation performance of the carbon membrane prepared from various types of polymer precursor membranes, polyimide-based carbon membrane shows the most promising performances. The defect-free carbon membranes can also successfully derived from polyimide membranes that can withstand the high temperature treatments and without softening and decomposing suddenly and rapidly. These materials can produced carbon membrane with high carbon yields and sustained their structural shapes after high temperature pyrolysis due to its incredible nature of strong and astounding heat and chemical resistance. Therefore, further studies on the preparation of carbon membrane from polyimide polymer need to give more attentions in the future, since this polymer are versatile plastics that can synthesize from a variety of dianhydride and diamines monomers. The chemical modification such as sulfonation, acidification and cross-linking on the original polyimide are also can be used to further alter the structural properties of the polyimides. In other words, polyimide-based carbon membranes can be designed and fabricated in a variety of chemical structures with distinct physicochemical properties corresponding to a specific separation task.

However, these kinds of polyimide are not acceptable in term of cost issues. The modification of polyimide through polymer blending is one of
the most cost effective and simple methods in tailoring the structure and properties of the resultant materials. This technique was carried out by the addition of the thermally labile polymer such as PVP or PEG, or inorganic materials such as silica, zeolite or carbon molecular sieves. Thus, pairing of the suitable polymers for a blend is a major challenge to produce carbon membrane with desired properties for gas separation application. In addition, a defect-free carbon membrane with homogeneous dispersion of inorganic materials is not an easy task. Most of the carbon membranes were prepared in the form of flat sheet and supported membranes, which have much less economic value. Therefore, the fabrication of these membranes in other configurations, especially hollow fiber should be performed due to the separation and cost effective as compared to other types of configurations.

From an industrial point of view, the carbon membranes can be a potential material to replace the available polymeric membrane in the market if they can be produced readily and reproducibly. Although amorphous, they are endowed with a regular nanostructure that leads to a pore network with narrowly distributed pore dimensions between 0.3 and 0.6 nm. Thus, further study on the preparation factors is crucially needed to obtain reproducible carbon membrane with high separation efficiency. An extensive study has been done by Shiflett and Foley (92) by measuring the carbon mass per area added several times onto the tubular support to get a reproducible supported carbon membrane. The results showed that the separation performance of a carbon membrane seems to be very sensitive to preparation conditions, other than the total carbon mass and application of the polymer onto the support. Therefore, other approach taken by this review is to discuss in detail on the influence of the preparation factors on the separation performance of the carbon membranes.

STABILIZATION PROCESS

Stabilization or pre-oxidation process is one of the steps involved in the fabrication of carbon membrane and is carried out before the pyrolysis process. Most of the prepared high performance carbon membranes have been successfully stabilized in air atmospheres between 150 and 460°C, depending on the type of polymer precursor used. It is believed that greater stability membranes are obtained after stabilization under air atmosphere mainly due to the contribution of oxygen in the dehydrogenation reaction. In fact, oxygen mainly acts as a dehydrogenation agent in the conversion of C-C bonds to C=C bonds and generates oxygen-bearing groups in the polymer backbone, such as –OH and C=O. These kinds of groups promote intermolecular cross-linking of the polymer chains and provide greater stability to sustain high temperature in the subsequent pyrolysis process. If the stabilization process is not completed throughout the entire membrane cross-section, a
significant weight loss can occur at higher temperature (44). The stabilization conditions applied by previous researchers are tabulated in Table 2. 

Besides that, the stabilization process offers the potential to prevent the melting and fusion of the polymeric membranes and avoid excessive volatilization of carbon element in the subsequent pyrolysis process (73). As a result, the final carbon yielded from the precursor can be maximized (10). Moreover, Zhang et al. (61) had suggested that the stabilization process should be conducted in order to maintain the morphological structure of thermoplastic polymer precursor in the resultant microporous carbons after heat treatment. Stabilization of the thermoplastic polymers in air allows oxygen bridges to be created between aromatic molecules that inhibit the rearrangement and growth of aromatic crystallites during pyrolysis step. Thus, a pore structure with more open pores can be formed in the resultant carbon membranes (105).

The stabilization process variables can significantly affect the performance of the resulting carbon membrane. These variables include stabilization temperature, heating rate and thermal soak time. The effect of stabilization temperature and thermal soak time are reported most frequently in the literature because an excess oxidation abruptly expands the pore size and decreases permeselectivity for permeants larger than 0.4 nm. A number of studies have also been done to optimize these process conditions to obtain carbon membrane of good performance (44, 47, 61, 72, 73). It was reported that the gas permeability and selectivity of the stabilized membranes were markedly increased in magnitude compared to the precursor membranes, due to the formation of pore structure by crosslinking and volatilization of small gaseous molecules produced by minor thermal degradation during stabilization. Additionally, as the stabilization temperature increased, the degree of decomposition and cross-linking in the membrane increased, which resulted in different micropore structures of the carbon membranes that can be used to tune gas separation properties of the derived carbon membranes.

The degree of cross-linking in the precursor membrane obtained during stabilization process is normally was determined by the dissolution test. For instance, the stabilized PPESK membranes that were carried out in air from 300 to 400°C were dissolved in NMP and some swollen pieces appeared. This indicates that some cross-linking structures had formed in this stage. Meanwhile, for stabilized membrane treated above 400°C, the infinite molecular weight made this membrane insoluble in NMP, suggesting that stabilization had proceeded sufficiently and the fully stabilized membrane had been achieved. The results showed that the gas permeabilities for all gases increased as the stabilization temperature was increased from 400 to 460°C. However, a low mechanical strength of stabilized membrane was obtained after being treated beyond 500°C, due to excessive oxidation. This revealed that the stabilization in air at high temperature can partially destroy
the original backbone of the polymer and also affect the developed pore system in the resultant carbon membrane (105). This work concluded that a suitable temperature is needed for stabilization of the polymeric precursor membrane, and can be determined based on the dissolution test and gas permeation measurement.

Coutinho et al. (44) studied the effect of stabilization temperature and thermal soak time on the final carbon membrane morphology. PEI/PVP membranes were heated to the maximum stabilization temperature of 250 and 400°C. The membrane was kept at these temperatures for 30, 60, and 90 min under air flow. The result showed that 400°C was a better temperature for stabilization process, where the oxidation reactions were more effective. It was evidenced by less deformation and irregularities in fibers. At the same stabilization temperature, the membranes with longer contact with air showed less cross-sectional deformation. Saufi and Ismail (10) indicated that stabilization process could be employed at different ranges of thermal soak times, depending on the precursor uses. In the case of carbon membrane made from PPESK, the stabilization process at high temperature could partially destroy the original backbone of the polymer. The maximum selectivity of the PPESK based carbon membrane was obtained from PPESK precursor oxidized at 460°C. The ideal selectivity for O₂/N₂, CO₂/N₂, and H₂/N₂ gas pairs were in the range of 10–14, 30–50 and 40–80, respectively (72).

The stabilization process performed in carbon membrane preparation is also similar to the stabilization process carried out in carbon fiber preparation. Basically, during the stabilization process, the precursor would undergo a number of physical and chemical changes due to a variety of exothermic chemical reaction, including decomposition, cyclization, dehydrogenation, oxidation, crosslinking and fragmentation. The cyclization reactions that convert PAN into an infusible stable ladder polymer are of most importance in PAN fibers (106). The stabilization reaction involved in the precursor polymer could be quantitatively estimated by means of FTIR spectroscopy.

For PAN polymer, these reactions such as cyclization, crosslinking and dehydrogenation were indicated by the observation of a new band at 1595 cm⁻¹. This band represented the combination vibration of C=C and C=N stretching, and NH in-plane bending of the ladder-frame structure of the stabilized PAN. Another band that contributed to stabilization of PAN fiber was at 1718 and 1660 cm⁻¹ due to the oxygen uptake reactions. Additionally, the 1595 cm⁻¹ band corresponding to cyclization became distinct only after PAN fiber was heated for 30 min in air atmosphere (107, 108). It was concluded that the effective stabilization reaction can only occur at certain temperatures under certain time of exposure in air environment.

So far, the scientific studies concerning the mechanism of the oxidation reaction during the stabilization step in the preparation of polymer based carbon membranes have not been clearly discussed in the literature. Most of
the studies reported in the preparation of these membranes were focused on
the effect of stabilization parameters on the gas permeation properties of the
carbonized membranes, in terms of permeability and selectivity rather than
on the chemical point of view. For instance, the mechanisms and kinetics of the stabilization reaction involved in PAN based carbon fiber have
been extensively studied. Therefore, similar studies on the mechanism of
the oxidation occurred in the preparation of stabilized polymeric precursor
membrane need to be identified in further details in the literature.

PYROLYSIS PROCESS

Pyrolysis process is the heart of carbon membrane production and can be
considered as a compulsory process. Generally, pyrolysis process under-
goes after stabilization process. According to Saufi and Ismail (10), pyrolysis
process is conventionally applied for the production of porous carbon
fibers, and causes the product to have a certain microporosity of molecular
dimensions that is responsible for the molecular sieve properties. Carbon
membranes can be produced by pyrolyzing various types of polymers under
various pyrolysis conditions. At the initial stage of pyrolysis process, most
chemical reaction and volatile emission occur. Typical volatile byproducts
produced are ammonia (NH₃), hydrogen cyanide (HCN), methane (CH₄),
hydrogen (H₂), nitrogen (N₂), carbon monoxide (CO), and carbon dioxide
(CO₂). The hydrogen evolution was indicated by the formation of graphite-
like structure. The evolution of these byproducts is dependent of the type
of polymer used and generally causes a large weight loss (10, 24).

During pyrolysis process, part of the heteroatoms originally present in
the polymer structure was eliminated while leaving behind a cross-linked
and stiff carbon matrix. As a result of the rearrangement of the molecular
structure of the starting polymeric precursor, an amorphous microporous
structure of carbon membranes was created by the evolution of gases (43).
The pore structure that formed during the pyrolysis process would deter-
mine the separation properties of carbon membrane. These pores were
non-homogeneous and consisted of relatively wide openings with a few
constrictions.

In general, the pores vary in size, shape and degree of connectivity
depending on the chemistry of its pyrolysis step and the morphology of the
polymer precursor. Figure 2(b) displays the idealized structure of a pore car-
bon material (24). Many researchers have reported that the microstructure
of carbon membranes (pore size, pore volume, and pore distribution) could
be tailored by controlling the conditions of pyrolysis process. Pyrolysis tem-
perature (also known as final temperature), heating rate, thermal soak time,
and pyrolysis atmosphere are among the factors that influence the pyrolysis
process. Therefore, it is necessary to optimize these parameters in order to
gain the best carbon membranes for gas separation. An overview of various pyrolysis protocols applied in previous studies are summarized in Table 2.

Pyrolysis Temperature

The parameter that gives a strong influence on the structure, separation performance and transport mechanism of carbon membranes is pyrolysis temperature. This variable depends on the type of the precursor utilized, and an increase in the pyrolysis temperature will lead to a decrease in gas permeability and an increase in selectivity (69, 109, 110). Pyrolysis is typically carried out at temperatures ranging from 500 to 1000°C, which are between the decomposition temperature and graphitization temperature of the precursor. The increase in pyrolysis temperature will produce carbon membrane with higher compactness, higher crystallinity, higher density and smaller average interplanar spacing between the graphite layers of the carbon (111).

Recently, Anderson and coworkers (50) studied the effect of pyrolysis temperature on the performance of nanoporous carbon membranes. They prepared supported nanoporous carbon membrane from PFA at various pyrolysis temperatures of between 400°C and 800°C for 2 h under Ar flow. The results indicate that the pore size decreases whilst the porosity increases with increasing pyrolysis temperature. A similar trend was observed for carbon membrane derived from polyimide (15, 30, 69), PEI (44, 45) and PPO (52).

In the case of phenolic resin precursor, it was observed that the pores appeared at approximately 500°C and enlarged up to 700 to 800°C. The pores finally disappeared when further heating to a higher temperature due to the pore shrinkage (57, 48). Centeno and Fuertes (66), have conducted an extensive study on determining the optimum pyrolysis temperature for carbon membrane based on phenolic resin. Experimental results showed that, pyrolysis temperature of around 700°C seems to be a good choice in the preparation of carbon membrane derived from a phenolic resin. A similar study has been successfully done by Lee et al. (78) where 700°C was estimated as an optimum temperature for the preparation of the PPO/PVP-based carbon membrane.

Some of the researchers pyrolyzed their precursor in a step-by-step heat treatment protocol before reaching the final pyrolysis temperature. Kusuki et al. (30), for example, fabricated asymmetric carbon membrane from polyimide precursor with three steps of heat treatment. The first step is the drying of the polyimide hollow fiber at 270°C in a N₂ atmosphere, the second is the stabilization at 400°C in air, and the third is the pyrolysis at over 600°C in N₂. The results indicate that, the permeability of H₂ decreased with an increase in the temperature of the pyrolysis. It is mainly due to the physical shrinking of the membrane with decomposition and chemical condensation of the
precursor and the evolution of the compounds. These carbon membranes displayed high membrane performance for the gas separation of H$_2$/CH$_4$ (100 to 630).

Preparation of carbon membrane at two different pyrolysis protocols using two different types of polyimide precursor was studied by Vu and Koros (69). These two protocols are different in pyrolysis temperature with the same heating rate and thermal soak time. Permeation results show that, carbon membranes produced from both precursors (Matrimid and 6FDA/BPDA-DAM) display similar CO$_2$/CH$_4$ selectivities (>70). Meanwhile, the CO$_2$ permeability of 6FDA/BPDA-DAM based carbon membrane is consistently 130% higher than that of carbon membrane from Matrimid.

These findings suggested that the identical pyrolysis protocol resulted in similar molecular-sieving and ultramicroporous morphologies, but created different larger-scale micropore regions in the two materials. In order to prepare carbon membrane with high permeability, pyrolysis process could also be performed at a constant temperature (temperature same as stabilization) instead of at elevated temperature. It is because, the pore formation is still occurring at this condition. The pores formed at this condition also were effective for O$_2$/N$_2$ and CO$_2$/CH$_4$ separation. This study has been reported by Nishiyama et al. (95) using supported polyimide carbon membrane from room temperature to 500$^\circ$C under N$_2$ flow. Similar studies were also found in other paper (37, 72).

According to these studies, pyrolysis temperatures are strongly depending on their type of polymer precursor membrane. It is recommended for the preliminary studies, the evolution of the structural morphology and gas permeation properties of the certain polymer precursor membranes should be carried out in order to understand their behavior during heat treatment process. The optimum pyrolysis temperature can be determined by treating the precursor membranes at various temperatures with certain interval systematically.

Heating Rate

Normally, pyrolysis is carried out at a wide range of heating rate of 1 to 13$^\circ$C/min (110). In order to obtain small pores and enhance the carbon crystallinity, lower heating rates are preferable. In contrast, higher heating rate may allow to the microscopic crack, pinholes formation, distortions and blisters. In this case, carbon membrane with low selectivity would form. Thus, an extensive study in determining an optimum heating rate for pyrolysis process must be done. This heating rate would determine the evolution rate of volatile components from polymeric membrane during pyrolysis (3). The effect of heating rate was investigated on carbon membrane derived from phenolic resin by performing pyrolysis process up to 700$^\circ$C at different heating rate. It was observed that the carbon
membranes produced at 0.5°C/min and 1°C/min presented quite similar separation characteristics. However, pyrolysis of phenolic resin film at 5°C/min notably reduced the gas permeability. This is because, the use of high heating rates for pyrolysis shifted the pore size distribution towards smaller pores and was beneficial for improvement of molecular sieve characteristics. When precursor membrane was pyrolyzed at 10°C/min, a more selective carbon membrane for separation of permanent gas pairs (O₂/N₂ = 5, CO₂/N₂ = 27, and CO₂/CH₄ = 23) and olefin/paraffin (C₂H₄/C₂H₆ = 3 and C₃H₆/C₃H₈ = 6) was obtained (48).

Besides, the fibers with cracks and defects on the external surface were obtained when the PEI membranes underwent pyrolysis process at a low heating rate of 1°C/min (44). On the other hand, Nishiyama et al. (70) suggested that the O₂ permeability strongly depended on the temperature of the pyrolysis rather than the heating rate. They also reported that the pyrolysis rate seemed greatly dependent on the membrane thickness. Therefore, to obtain reproducible permeation data, the membrane thickness should be controlled more precisely in the future. The most effective heating rate that has been applied in the preparation of the polymer-based carbon membrane is in the range of 1–5°C/min. But, it still depends on the type of polymeric precursor membranes used.

Thermal Soak Time

Thermal soak time during pyrolysis process can be different, depending on the final pyrolysis temperature (6, 48). Thermal soak time is the period of time taken to hold membrane at constant pyrolysis temperature before the membrane is cooled down to room temperature. This variable can be used to fine-tune the transport properties of carbon membrane. According to previous studies, selectivity of carbon membrane would increase at high thermal soak time (24, 35, 56, 110). Vu et al. (69) pointed out that only microstructural rearrangement occurred during the thermal soak time, thus influencing the pore size distribution and average porosity of carbon membrane. Centeno et al. (48) performed the pyrolysis process with soaking times between 1 and 8 h at 700 and 800°C. It was found that the carbon membrane kept at 700 °C for 1 h showed the best performance in terms of permeability–selectivity, while the membrane soaked for 6 and 8 h favored the rearrangement and subsequent alignment of carbonaceous aggregates. In addition, the increase in holding time to 8 h led to a carbon membrane mainly permeable to gases with a molecular size smaller than 4 Å and with excellent properties for O₂/N₂ and CO₂/CH₄ separation. In the case of carbon membrane pyrolyzed at 800°C, permeation results indicate that the soaking time of 1 h was sufficient to improve the permeability and poses a highly selective carbon membrane.
Pyrolysis Atmosphere

Pyrolysis process can be applied either in vacuum, inert atmosphere (He, N₂, or Ar) or oxidative atmosphere (CO₂). The chemical damage and undesired burn off of the polymer membrane precursor during pyrolysis can be avoided by controlling the pyrolysis atmosphere. Table 3 shows the pyrolysis atmospheres applied in carbon membrane preparation by various researchers. Two different modes of pyrolysis operation on polyimide hollow fiber membranes have been reported in the work of Vu and Koros (69). The pyrolysis processes were carried out under vacuum and inert gas (He). Permeation results showed that utilization of He gas instead of a vacuum environment during pyrolysis would increase CO₂ permeability, resulting in a significant loss of CO₂/CH₄ selectivity. The authors postulate that the inert gas environment accelerates the carbonization reaction through increased gas-phase heat and mass transfer to form a more open porous matrix. Similar findings were reported by Lua and Su (37), Su and Lua (40) and Centeno et al. (48).

It was observed that the membrane pyrolyzed under N₂ flow has better separation properties than those pyrolyzed under vacuum. This is because the pyrolysis under inert gas flow favored the volatile compounds release

<table>
<thead>
<tr>
<th>Pyrolysis media</th>
<th>Results</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>He</td>
<td>• Increase CO₂ permeance but resulted in a significant loss of CO₂/CH₄ selectivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• More productive but less selective</td>
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</tr>
<tr>
<td></td>
<td>• Form a more open porous matrix</td>
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</tr>
<tr>
<td></td>
<td>• High weight loss</td>
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</tr>
<tr>
<td></td>
<td>• High BET pore surface area, total pore volume, and micropore volume were obtained</td>
<td></td>
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<tr>
<td>N₂</td>
<td>• High gas permeability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Accelerate the carbonization with temperature increase for which a more open porous structure were created</td>
<td></td>
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<tr>
<td>Ar</td>
<td>• Less weight loss</td>
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<tr>
<td></td>
<td>• High selectivity</td>
<td></td>
</tr>
<tr>
<td>Vacuum</td>
<td>• Low d-spacing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Smaller pore size</td>
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<tr>
<td></td>
<td>• Denser carbon structure formed</td>
<td></td>
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<tr>
<td></td>
<td>• Low gas permeability and high selectivity</td>
<td></td>
</tr>
<tr>
<td>Oxidative (CO₂)</td>
<td>• More permeable and high permselectivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High microporosity, total volume of pores and BET specific surface area</td>
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TABLE 3 Summary of Pyrolysis Atmosphere Applied by Various Researchers
during carbonization and avoided the carbon deposition in the pores already formed (48). Besides that, Lua and Su (37) experienced that the pyrolysis under vacuum is favorable for producing carbon membranes with high selectivity whilst pyrolysis under N$_2$ is favorable for preparing carbon membranes with high permeability. Similar results were also reported by Song et al. (62). Based on Su and Lua’s (40) experimental works, it was showed that the influence of pyrolysis atmosphere on the carbon membrane performance was more significant at the lower temperature. It is because, at higher temperature, the membranes have shrunk as evidenced by the reduced BET surface area and total pore volume and some pores have shrunk to such an extent that they were no longer permeable to the gas molecules.

Furthermore, Favvas et al. (38) prepared 3 different kinds of carbon hollow fiber membranes using 3 different pyrolysis media (N$_2$, N$_2$ saturated with water, CO$_2$), at a final temperature of 900°C. The results revealed that membranes prepared in CO$_2$ environment were more permeable and exhibited high permselectivity than those pyrolyzed in N$_2$ and N$_2$ saturated with water. For instance, the highest selectivity value for the H$_2$/CH$_4$ pair (138) was obtained for the membrane pyrolyzed under CO$_2$ atmosphere. The authors concluded that the application of a reactive media could result in carbon structures with higher microporosity, total volume of pores and BET specific surface area. Recently, pyrolysis process using a mixed gas containing specific amount of O$_2$ (4, 8, 30, or 50 ppm) in inert (He and Ar) was performed by Kiyono and coworkers (67) using 6FDA/BPDA-DAM as a precursor.

The findings clearly reveal that a strong relationship exists between the total amount of oxygen and the transport properties, especially performances among inert pyrolysis. Selectivity increases and permeability decreases as the amount of oxygen in the inert gas increases. Besides, when dealing with the inert gas pyrolysis system, the inert gas flow rate also needs to be considered. The increments in gas flow rate will improve the permeability of carbon membrane without significantly affecting their selectivity (56, 109).

The identical pyrolysis protocol may result in different morphologies and separation properties for different polymer-based carbon membranes. In conclusion, a critical study on the effect of each heat treatment parameter from stabilization to pyrolysis step is very important in order to obtain an optimum pyrolysis protocol. The pore structures and properties of the resultant carbon membranes can be finely adjusted to a desired separation task through heat treatment process, especially by controlling their process temperature. Hence, matching of desirable carbon membranes performance properties with proper pyrolysis protocol is very imperative for the fabrication of high performance carbon membranes.
CARBON MEMBRANE CONFIGURATIONS

In practice, carbon membranes have been fabricated in two main configurations which are unsupported membranes (flat membranes, capillary tubes or hollow fibers) and supported membranes (flat or tubular) on a macroporous material (41, 44). As a support, sintered metals, alumina, or graphite like materials can be used either in flat disk or tubular configurations. There are several methods to deposit the polymer solution on the support such as dip-coating (32, 42, 48, 57), spin coating (34, 41, 50, 55, 66), spray coating (79) and ultrasonic deposition.

To date, numerous types of supported and unsupported carbon membranes have been tested for gas separation and reported in the literature. The supported carbon membrane is the most popular and simpler configuration that have been studied by various researchers. However, this type of configuration exhibits a problem in depositing polymer solution on the support uniformly. The cycle of polymer deposition-pyrolysis needs to be repeated several times in order to obtain an almost defect-free membrane (31, 50, 64).

Nevertheless, the number of reports on hollow fiber carbon membrane increased in 2000s and most of them are prepared from polyimide-type precursor. The main beneficial features that contribute by hollow fiber are high separation efficiency, high active surface area to volume ratios (>1000 m²/m³), able to operate at high pressure drops and low production cost as compared to other types of configuration (28, 56). The challenge of hollow fiber carbon membranes for practical use is their poor mechanical properties (brittleness), since they are self-supporting.

CHALLENGES IN CARBON MEMBRANES PREPARATION

As mentioned before, most of the inorganic membranes, especially carbon membranes are still in the scientific research stage. The high cost of materials, complex synthesis procedure and low productivity as compared with polymeric membrane has placed carbon membranes on the brink of commercialization. The typical current price for polymer membranes is $20/m² in a module configuration with A_m/V_mod 1,440 m²/m³ (112). Besides the cost issue, there are other challenges that are still in research progress, such as the mechanical, chemical and physical stability of the membranes.

Mechanical Stability

The mechanical properties of the membrane are essential in operation and module design. In the case of carbon membranes fabricated by pyrolysis of
polymeric membrane, the major disadvantage that hinders their commercialization is their brittleness, which means that they require careful handling. In 1999, Tanihara and coworkers (33) studied the mechanical property of the carbon membrane derived from asymmetric polyimide hollow fiber membrane produced by UBE Industries. The elastic modulus significantly increased and the breaking elongation decreased as the heat treatment temperature increased from 600 to 1000°C. The elastic modulus of the resultant carbon membrane pyrolyzed at 800°C shows 9 times larger than those treated at 270°C. It was demonstrated that the aromatic fragments’ growth and crosslinking between the fragments progressed during the heat treatment process. It was also due to the asymmetric structure of the membranes becoming dense with increasing heat treatment temperature. The similar trend towards the increase in elastic modulus of the carbon membranes was also found in polyacrylonitrile-based carbon fiber studies (113, 114).

In 2002, an early work on the preparation of flexible carbon membrane from sulfonated polymer was studied. Okamoto’s research groups (115, 116) modified polyimide polymer into sulfonated polyimide by the introducing sulfonic groups in the original polymer. The precursor membranes were then pyrolyzed at low temperature of 450°C for 1.5 h. The results indicated that carbon membranes prepared at low pyrolysis temperature have the ability to separate C₃H₆/C₃H₈ and CO₂/N₂ gas pairs with high selectivity. While at pyrolysis temperature of 500°C, the derived carbon membranes were brittle and the gas permeation measurement could not be performed. In addition, the gas permeability increased as the content of sulfonic groups added increased. It is because the spaces occupied by these groups might be left as microvoids in the membrane structure after the pyrolysis process.

Recently, a flexible carbon membrane derived from sulfonated poly(phenylene oxide) was successfully prepared by Yoshimune and Haraya (117). The mechanical property of this membrane was measured by means of a bending test technique on the glass tube. It was found that pyrolysis of carbon membrane in the range of 450 to 600°C produced a more flexible carbon hollow fiber membrane with a smaller bending radius. In contrast, for carbon membrane pyrolyzed at 700°C, a less flexible and brittle carbon membrane was obtained due to the shrinkage effect during pyrolysis. The outer diameter of the hollow fiber prepared also affected the mechanical property of the resultant carbon membranes, and the bending radius increased with the increasing of the carbon membrane’s outer diameter.

In addition to these issues, Ismail et al. (9, 10) stated in their review that the brittleness problems can be minimized by utilizing PAN as a precursor membrane for carbon membrane, since this polymer have been widely used in the production of high strength carbon fiber. Further studies on the preparation of carbon membrane with high mechanical properties would be a major breakthrough in this field and give an opportunity for commercialization. There are probably some available polymers and modified polymers
that have the potential to produce carbon membrane with mechanical sta-

bility that fulfils the industrial qualifications. Besides, some modifications of

the techniques used in the preparation of carbon membrane can also tackle

this problem.

Based on the author’s knowledge, details on the mechanical proper-

ties of the carbon membrane are still lacking in the literature. One of the

problems is the experimental operation of this membrane’s fragility. For

brittle carbon membranes, the breaking elongation is relatively short, even

at a long gauge length; the membrane elastic modulus is also high, so the

wrong recording of the elongation to the membrane must occur once there is

motion deformation in the initial stretching. There are various types of dam-

age to the membrane in the sample preparation and testing process, such

as picking a carbon hollow fiber membrane from a bundle, mounting the

membrane sample to the tensile machine, and adhering the membrane to a

paper holder. Although these membranes have poor mechanical properties,

it is still capable of being constructed into the module for gas permeation

testing in the laboratory scale; and manifold studies on the gas permeation

performance of the carbon membrane have been reported in the literature.

Chemical Stability (Oxidation of the Membrane)

The membrane operational stability is obviously related to the occurrence of

unwanted chemical reaction. Carbon membranes present significant prob-

lems regarding their performance stability, although they exhibit excellent

chemical and thermal resistance. One of the problems faced by carbon mem-

branes is their vulnerability to oxidation. The permeation properties of the

membranes would drastically affect even a small change in the size of pore

constrictions, and the associated changes can be quite significant on time

scales of weeks to years (118, 119).

When exposed to air (even at room temperature), oxygen atoms from

air combine with some active sites and create oxygen surface groups. Thus

oxygen chemisorptions can eventually reduce the open porosity towards

gas transport and increase the number of constrictions of the pore structure,

offering additional restriction to diffusion, which is known as carbon aging.

During aging, the rate of change in permeation properties is dependent on

the size of the gas molecules and it is significantly affected by the permeation

of larger molecules due to the loss of free volume (119, 120).

An extensive study was conducted by a research group from Japan (32,

121) to investigate the effect of oxidation on the gas permeation of the poly-
imide based carbon membrane. For carbonized membrane prepared under

oxidation in O2-N2 mixtures, the permeances of all gases increased, espe-

cially for molecules larger than 0.4 nm due to the broadening of the pore

size distribution. Oxidation of pore walls was also found to possibly enhance

the adsorption of polar molecules. The stability of the carbonized membrane
was then investigated by maintaining this membrane in air at 100°C for one month. In the meantime, the permeation properties were systematically measured. During this treatment, oxygen in air reacted with the membrane and formed oxygen-containing functional groups, which continuously decomposed to CO₂. This was indicated by the changes in elemental contents of the membrane after the oxidation process. In the initial stage of the oxidation, the permeability of larger molecules was considerably decreased, but it was restored after the regeneration step.

Later, the effects of aging on carbon membrane permeation properties associated with air oxidation were studied by Fuertes and Menendez (47, 120). The derived carbon membranes were stored under various types of environments such as dry air, humid air, propylene and nitrogen. The results showed that a rapid loss in permeability with time was observed for carbon membrane stored in dry and humid air. In contrast, carbon membranes stored under propylene and nitrogen were protected from damage.

It is considered that oxygen chemisorptions into carbon membranes instead of water physisorption is the main reason for the loss of permeability when a prepared carbon membrane is exposed to air. These findings are in agreement to the results reported recently by Lagorsse and coworkers (122). These drawbacks seriously limit the application of carbon membranes to air separation. Based on these results, it can be suggested that the use of carbon membranes is more feasible in oxygen-free gas mixtures such as alkene/alkane, hydrocarbon isomers, H₂/hydrocarbons and N₂/hydrocarbons. In order to remove the oxygen surface groups, an aged carbon membrane resulting from exposure to pure oxygen or air was heat treated in a reducing atmosphere at 893 K. After this treatment, the O/C ratio in the carbon membrane decreased by 22%. However, it was found that chemisorptions of oxygen in this membrane is irreversible and still leaves a surface containing reactive carbon sites capable of re-adsorbing oxygen at room temperature.

To protect and minimize the carbon membrane from aging damage, the regeneration technique by exposure to pure propylene was proposed in 1994. Experimental results demonstrated that most membrane recovery cases were significantly boosted by exposure to propylene and it was confirmed that this chemical is effective in removing absorbed groups. The exposures to propylene completely restored the membrane shut down by hexane to its original condition in terms of selectivity and O₂ permeability. During regeneration, the adsorbed compounds were easily removed from the carbon probably due to the weaker interaction forces on the pore wall of the carbon membrane. However, regeneration attempts with propane, ethylene, and 1,3-butadiene have all been unsuccessful (123). Besides acting as regeneration agent, propylene can also be used for storage purpose of the carbon membranes as suggested by Menendez and Fuertes (120). In contrast, propyne was used as alternative cleaning agent in Lagorsse’s (122)
work, but no significant membrane recovery was measured. In addition, the surface oxides formed by oxidation in air for a long-term period could also be eliminated by heat treatment in inert gas at high temperature (121).

Besides that, oxidation process has also been performed as a post-treatment process in carbon membrane preparation. This process, known as post-oxidation, is the popular post-treatment utilized in previous studies to adjust the pore structure of the derived carbon membrane. Generally, the average pore size would increase when a membrane is exposed to an oxidizing atmosphere after the pyrolysis process. An oxidizing atmosphere can be pure oxygen, oxygen mixed with other gases, or air (10). In recent years, the post-oxidation effect on the permeation performances of the carbon membrane under different oxidation conditions have been extensively studied by Lee’s research group (51, 53, 54).

After the pyrolysis process at 700°C in Ar atmosphere, the carbon membrane was subjected to oxidation process at different temperatures (100°C to 400°C) and time (30 min to 3 h) for the modification of the gas permeability in the PPO derived carbon membrane. The heating and cooling rate for the oxidation was set to 5°C/min in the air condition. Large increases were observed in the permeation results of the gas species with large kinetic diameter (N₂ and CH₄) and the N₂ and CH₄ permeability of oxidized carbon membranes were increased by about 3 to 5 and 4 to 9 times, respectively.

In the case of gases with small kinetic diameters (He and CO₂), the permeability increased only about 2 to 3 times for oxidized carbon membranes. The permeation results implied that the air oxidation increased the pore size and the pore volume of the carbon membrane with increasing oxidation temperatures. The selectivity of all gas species were significantly decreased, as compared with the results of the non-oxidized carbon membrane.

Regarding the influence of the oxidation time on the permeation performance, they found that the oxidation process enlarged the membrane pore with increasing oxidation time and widened the membrane micropores at longer oxidation times. A low oxidation temperature (200°C) and somewhat shortened time (1 h) was determined as the optimum oxidation condition. Moreover, Fuertes and Menendez (47) also applied post-oxidation process in their research in order to improve the separation properties of the carbon membranes.

To date, papers regarding the systematic studies on the stability and durability of the derived carbon membranes are still not sufficient to be used as a reference. According to previous studies, it was suggested that besides regeneration techniques using cleaning agents such as propylene or propyne, a stabilization step is also needed after the production. This is because the main characteristic for membrane to be used in industrial scale is durable for a long-term process. Therefore, further research on this treatment is needed in order to minimize the vulnerability of the carbon membrane to oxidation.
Physical Stability (Sorption of Trace Components)

In general, carbon surfaces are hydrophobic but micropore walls of carbonized membrane are partially covered with oxygen-containing functional groups, thus giving the membrane a hydrophilic character. Once the first water molecule is adsorbed, adsorbate-absorbate interactions promote the adsorption to further molecules through hydrogen bonds (124). It has been reported that the selectivity of a typical membrane decreases as the amount of sorbed water increases. This is primarily due to the fact that water vapor can be found in a large number of process streams. Not many studies have taken into account this phenomenon very seriously; however, this problem has become crucial under real-world operations.

One of the approaches to this problem is the coating method with highly hydrophobic polymer to develop carbon composite membrane (125). The composite membrane was designed to have high resistant to water vapor to prevent a decrease in permeation flux. On the other hand, the humidity found in the ambient atmosphere can also give an adverse effect to the carbon membrane. Thus, the study of storage conditions for carbon membranes is also an important consideration for carbon membrane research in the future. The vulnerability of carbon membrane to humidity is a complex phenomenon, considering the weak character of the water-carbon dispersion forces and the tendency of water molecules to form hydrogen bonds within the bulk phase (120, 124).

Although these membranes have demonstrated exceptional separation properties with highly purified feed gases, the basic nature of the carbon itself makes these membranes vulnerable to compounds typically found in industrial process streams. Carbons generally make them excellent adsorbents for removing organics from process streams, but result in significant problems in membrane processes. Carbon membrane performance losses in terms of selectivity and permeability are severe and appear to have a finite loading capacity for organic adsorption. This trend has been observed for a number of different organic compounds.

A large volume of research exists regarding the nature of sorption in carbon materials and it is well established that sorption in carbons is related both by the chemical nature of the carbon and by its porous structure (126–128). Due to higher interaction potentials resulting from the close proximity of pore walls, the sorption in micropores is enhanced. Based on the adsorption properties of organics in microporous carbons, it is believed that ultramicroporous carbon membranes would be very vulnerable to adverse effects from exposure to organic compounds. Numerous researchers have found that although the sorption mechanisms may vary, organic compounds generally have a very high affinity for carbon adsorbents.

Membrane performance losses in terms of selectivity and flux are severe, and occur with feed stream concentrations of organics as low as
0.1 ppm. Moreover, carbon membranes have limited stability in some gases (CH$_4$, H$_2$, CO$_2$, O$_2$) at relevant temperatures and appear less feasible for pre-combustion decarbonization processes (129). Therefore, the modification of the carbon membrane in terms of surface properties is a key technology in producing carbon membranes with high performance stability.

**CONCLUSION AND FUTURE DIRECTION**

Today, membrane processes are employed in a wide range of applications and the number of such applications is still growing. Several gas separation applications have been commercially applied. Until now, the largest industrial gas separation application is natural gas process. The total worldwide consumption of natural gas is approximately 95 trillion standard cubic feet a year. This consumption drives a worldwide market for new natural gas separation equipment of USD 5 billion/year and membrane processes have less than 5% of this market (130). Carbon membranes have appeared as one of the most popular topics among the membrane researchers due to its spectacular separation performance. However, an intensive research and development work should be carried out to make the carbon membranes of industrial reality.

An increase in the activities of carbon membrane research and a great separation performance of the carbon membrane will be the principal motivation in the near future. The carbon membrane will become another alternative material used for industrial separation process due to this outstanding role in gas separation process. The results of carbon membrane performance that have been reported by different investigators are shown in Table 4.

Among the polymer precursors that have been discussed earlier, polyimides are the ones with the largest volume of research. It is due to their superior gas transport properties, good physical properties, and high thermal and chemical stability. However, the use of modified and blending polymer has become one of the prospective technologies for the current carbon membranes separation processes. The incorporation of thermal labile polymer and inorganic material (zeolite, silica, and carbon nanotube) in polymer solution has improved the transport properties of the resultant carbon membrane significantly.

It has been agreed that process parameters such as stabilization temperature, pyrolysis temperature, heating rate, thermal soak time, and gas atmosphere are the important parameters that should be taken into consideration during heat treatment process. This is because these parameters will affect the pore properties of the resultant carbon membrane, which determine the membrane separation mechanism. Thus, by optimizing these parameters, a high-performance carbon membrane for gas separation can
<table>
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(Continued)
**TABLE 4 (Continued)**

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<td>SPAEK/H</td>
<td>28</td>
<td></td>
<td>228</td>
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<td>SPAEK/Na</td>
<td>16</td>
<td></td>
<td>175</td>
<td></td>
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be produced. All the experimental data that are obtained should be simulated using computer software to achieve an ideal and practical pyrolysis condition that can be implemented on a pilot scale.

Most of the research on carbon membrane has concentrated on the O\textsubscript{2}/N\textsubscript{2} separation. The study of this gas mixture is not an easy task because of the smaller difference of the gas kinetic diameters (O\textsubscript{2} = 3.46 Å; N\textsubscript{2} = 3.64 Å). In the literature, various reports on O\textsubscript{2}/N\textsubscript{2} separation using carbon hollow fiber membranes and supported carbon membranes are available (35, 37, 39, 45, 47, 48, 57, 59–61, 15, 65, 70, 72, 76, 77). This gas pair separation can be applied in air separation, oxygen-enriched air for combustion processes, medical purposes and pure O\textsubscript{2} and N\textsubscript{2} production. Power plants combined with coal gasification processes need a hydrogen separation step at about 300–500°C. In that high temperature operation, only a pressure driven membrane separation process can isolate the H\textsubscript{2} from other carbon compounds (CO\textsubscript{2}, CO). However, organic polymeric membranes cannot resist very high temperatures and begin to decompose with certain components. Thus, in this case, inorganic carbon membrane that is chemically inert and thermally stable up to more than 500°C is more suitable for this application (42, 66, 133).

In addition, carbon membrane also has a potential to recover CO\textsubscript{2} gas from power plants that burn fossil fuel and to avoid its emission to the atmosphere. This application was recommended by Centeno and Fuertes (66), when they had successfully prepared carbon membrane with high selectivity of CO\textsubscript{2}/N\textsubscript{2}. Similar findings were also made in the studies of Fuertes and Menendez (47), Lua and Su (37), Powell and Qiao (134), Zhang et al. (103), Favvas et al. (38), Rao et al. (45) and Liu et al. (72).

The other typical applications of CO\textsubscript{2} separation include the processing of reformate mixtures and the upgrading of biogas and landfill gas (42). Carbon membrane also can be applied for the separation of alkenes/alkanes and olefins/paraffins gas mixtures (15, 64). Hayashi et al. (135, 136) have prepared supported polyimide carbon membrane and reported that good separation performance for the separation of ethylene/ethane and propylene/propane mixtures can be achieved. Later, Okamoto et al. (137) examined olefins/paraffins separation by using asymmetric hollow fiber polyimides carbon membrane. Fuertes and Menedez (47) have prepared phenolic resin based carbon membrane for olefins/paraffins and n-butane/iso-butane separations. Besides that, the possibility to separate isomers of hydrocarbons between normal and branched polymers has been noticed by Soffer et al. (138).

Moreover, Itoh and Haraya (139) have concluded that the performance of the carbon membrane reactor for the dehydrogenation of cyclohexane to benzene was fairly good compared with that of a normal reactor. On the other hand, Lapkin (140) used a macroporous carbon membrane based on phenolic resin as a contactor for hydration of propane in catalytic reactors.
He found that the use of this porous contactor reactor for high-pressure catalytic reaction was of practicable usefulness. In 2003, Coutinho et al. (44) claimed that the PEI-based carbon membranes had a potential to be applied in catalytic reactor application.

Other applications of carbon membrane are for separation and recovering halogen compounds from mixtures of halogen compounds and carrier gases (N₂, etc.) in gas-utilizing semiconductor processes for etching and rinsing (141), enriching hydrogen streams containing C₁-C₄ hydrocarbon mixtures (142) by surface selective membrane carbon membrane, and in the medical field (virus, proteins, bacteria) and food industry (liquid clarifications - liquors, soy sauce, soft drinks, vinegar) separations (143).

The great potential and numerous advantages of carbon membranes will definitely lead to their wide applications in the gas separation industry over the coming years. It is believed that gas separation technologies by carbon membrane will break through the limitation and the weaknesses of available polymeric membranes. It is hoped this review can serve as a scientific platform for researchers and engineers to develop a viable and practical carbon membrane for gas separation processes in the future.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support under National Science Fellowship (NSF) from the Ministry of Science, Technology and Environment of Malaysia.

ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>ZSM-5</td>
<td>Zeolite Socony Mobil-five</td>
</tr>
<tr>
<td>LTA</td>
<td>Linde Type A</td>
</tr>
<tr>
<td>PI</td>
<td>Polyimide</td>
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<tr>
<td>BPDA</td>
<td>3,3′,4,4′-biphenyltetracarboxylic dianhydride</td>
</tr>
<tr>
<td>BPDA-pPDA</td>
<td>3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), p-phenylenediamine (PDA)</td>
</tr>
<tr>
<td>BPDA-pp’ODA</td>
<td>3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), 4,4’-oxydianiline (ODA)</td>
</tr>
<tr>
<td>6FDA/BPDA-DAM</td>
<td>4,4’-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), 2,4,6,-trimethyl-1,3-phenylene diamine (DAM)</td>
</tr>
<tr>
<td>PBI</td>
<td>Polybenzimidazole</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyetherimide</td>
</tr>
<tr>
<td>PAN</td>
<td>Polycrylonitrile</td>
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<tr>
<td>PFA</td>
<td>Polyfurfuryl alcohol</td>
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</table>
PPO Polyphenylene oxide
TMSPO Trimethylsilyl substituted polyphenylene oxide
PVDC Poly (vinylidene chloride)
PVDC-PVC Poly (vinylidene chloride-co-vinyl chloride)
PFR Phenol formaldehyde resin
PPES Poly(phthalazinone ether sulfone)
PPESK Poly (phthalazinone ether sulfone ketone)
SPAEK Sulfonated poly (aryl ether ketone)
PVP Polyvinylpyrrolidone
PEG Polyethylene glycol
CMS Carbon molecular sieve
MWCNTs Multiwall carbon nanotubes
PI-BTCOOMe Bis(phenyl)fluorene-based cardo polyimide
Cs$_2$CO$_3$ Cesium carbonate
O$_2$ Oxygen
N$_2$ Nitrogen
CO$_2$ Carbon dioxide
CH$_4$ Methane
H$_2$ Hydrogen
He Helium
C$_2$H$_4$ Ethene
C$_2$H$_6$ Ethane
Ar Argon

REFERENCES


