[Review Paper]

Gas and Vapor Separation through Polyimide Membranes

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Organic, inorganic, and metal-based materials for membrane technologies have been studied and developed, and membranes made from some of these materials have been applied to industrial applications. Various polyimides synthesized from combinations of several types of acid dianhydrides and diamines allow systematic molecular design of the membrane materials. Polyimide membranes applied to hydrogen recovery in the petroleum industry in the 1980s are still used in various applications for gas and vapor separation such as nitrogen- or oxygen-enrichment by air separation, dehumidification, dehydration, carbon dioxide removal, and others. In particular, polyimides from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) have excellent fiber-forming properties with good thermal, chemical, and mechanical durability, so are used to manufacture asymmetric hollow fiber membranes for use in many membrane separation processes. This review introduces the material characteristics of polyimides, membrane properties of polyimide hollow fiber membranes, and applications as membranes for gas and vapor separation.

Keywords
Membrane, Gas separation, Vapor separation, Permeation, Polyimide, Hollow fiber

1. Introduction

Membrane separation systems are based on the research and development of membrane materials, membranes, membrane modules, and membrane systems, and combine these various technologies. The main characteristics required for membranes with gas and vapor separation properties are shown in Table 1. The properties of permeability and selectivity for gases and vapors of membrane materials have been summarized elsewhere1). Good permeability and good selectivity are important for effective membrane materials. However, ease of processing is more important for membranes that can be applied to practical uses and industrial applications. In particular, the membrane materials must have characteristics that allow the formation of thin layers, the forming of hollow fiber membranes, and the assembly into membrane modules, and so on. Empirically, many membrane materials are available with good permeability and good selectivity for gases and vapors but few membrane materials have suitable characteristics for introduction into industrial applications.

Polyimides have been widely reported as membrane materials with suitable properties for gas and vapor separation2)–25). In particular, polyimides from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) have excellent fiber-forming characteristics for the manufacture of asymmetric hollow fiber membranes with good thermal, chemical, and mechanical durability.

2. Permeability Coefficients of Membrane Materials

The permeability of membrane materials is defined by the permeability coefficient measured as the permeation volume of gases and vapors per unit membrane thickness, per unit membrane area, per unit time, and per unit driving force of pressure. The unit of the permeability coefficient is the Barrer, where 1 Barrer = 1 × 10−10 cm3(STP) cm cm−2 s−1 cmHg−1. The selectivity of membrane materials is expressed as the ratio of the permeability coefficient of a gas or a vapor to that of...
other gas or other vapor. Gas permeation in a non-porous type polymeric film is controlled by the solution-diffusion mechanism. The permeability coefficient is expressed as the product of solubility coefficient and diffusion coefficient. The unit of the diffusion coefficient is cm² s⁻¹ and that of the solubility coefficient is cm³(STP) cm⁻³ cmHg⁻¹.

**Figure 1** shows the chemical structure of polyimides made from various acid anhydrides and diamines. Polyimide films with thickness of 0.007 to 0.20 mm were prepared by (a) casting polyimide solution in a solvent on a flat plate, evaporating the solvent, and heat-treating the remained film, or (b) casting polyamic acid solution in a solvent on a flat plate, evaporating the solvent, and imidizing by heat-treating the remained film\(^{16,17}\).

**Table 2** shows the glass transition temperature and permeability coefficient and diffusion coefficient of gas and vapor. The order of glass transition temperatures is PMDA-based polyimide > 6FDA-based polyimide > BPDA-based polyimide. The order of the permeability coefficients is 6FDA > PMDA > BPDA. The order of the selectivity is BPDA > PMDA > 6FDA.

<table>
<thead>
<tr>
<th>Films</th>
<th>(T_g) [^{[\circ C]}^{}]</th>
<th>Permeability coefficient [Barrer]</th>
<th>Selectivity</th>
<th>Diffusion coefficient [10⁻¹⁰ cm² s⁻¹]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(H_2O)</td>
<td>He</td>
<td>CO₂</td>
<td>O₂</td>
<td>N₂</td>
</tr>
<tr>
<td>BPDA-DADE</td>
<td>270</td>
<td>780</td>
<td>0.642</td>
<td>0.188</td>
<td>0.023</td>
</tr>
<tr>
<td>6FDA-DADE</td>
<td>287</td>
<td>2160</td>
<td>33.8</td>
<td>13.8</td>
<td>2.93</td>
</tr>
<tr>
<td>PMDA-DADE</td>
<td>420</td>
<td>1510</td>
<td>3.2</td>
<td>0.858</td>
<td>0.171</td>
</tr>
<tr>
<td>BPDA-TSN</td>
<td>-</td>
<td>3100</td>
<td>12</td>
<td>2.7</td>
<td>0.577</td>
</tr>
<tr>
<td>6FDA-TSN</td>
<td>-</td>
<td>104</td>
<td>56</td>
<td>14.2</td>
<td>2.82</td>
</tr>
<tr>
<td>BPDA-DADM</td>
<td>292</td>
<td>4.6</td>
<td>1</td>
<td>0.21</td>
<td>0.03</td>
</tr>
<tr>
<td>6FDA-DADM</td>
<td>296</td>
<td>33</td>
<td>15.1</td>
<td>3.2</td>
<td>0.563</td>
</tr>
<tr>
<td>PMDA-DADM</td>
<td>-</td>
<td>3.95</td>
<td>0.99</td>
<td>0.205</td>
<td>0.033</td>
</tr>
<tr>
<td>BPDA-CMD</td>
<td>308</td>
<td>6.9</td>
<td>0.98</td>
<td>0.26</td>
<td>0.031</td>
</tr>
<tr>
<td>6FDA-CMD</td>
<td>-</td>
<td>30</td>
<td>6.8</td>
<td>10.3</td>
<td>2.13</td>
</tr>
<tr>
<td>BPDA-PASN</td>
<td>290</td>
<td>1600</td>
<td>7</td>
<td>1.75</td>
<td>0.35</td>
</tr>
</tbody>
</table>

\(T_g\) is glass transition temperature.
3. Permeance of Membranes

Polyimide hollow fiber membranes were prepared by extruding polyimide solution into a cylindrical shape from a nozzle, extracting the solvent in the coagulation bath containing a poor solvent, and drying and heat-treating the wet polyimide hollow fiber.

**Figure 2** shows scanning electron microscopy (SEM) photographs of the cross-section of the asymmetric polyimide hollow fiber membrane. In general, the outer diameter of the hollow fiber is 0.2 to 0.8 mm, the inner diameter is 0.1 to 0.7 mm, and a thin skin layer (dense layer) of 50 to 200 nm in thickness is present on the outer surface of a porous support layer.

Shape control of the hollow fiber membrane as shown in **Fig. 2**, thickness control of the skin layer on the outer surface, and asymmetric structure control of the porous support layer were not easy. Furthermore, improvements in productivity and cost performance for practical uses were also not easy. However, some suitable combinations of polyimides, special solvents and poor solvents were identified, and spinning techniques were developed, allowing practical applications of the polyimide separation membrane.

**Figure 3** shows examples of the gas and vapor permeation properties of polyimide hollow fiber membranes. The permeability of membranes for practical uses is defined by permeance with a unit of cm$^3$(STP) cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$. Permeance is defined as the ratio of permeability coefficient to the membrane thickness. The selectivity of membranes is expressed in the ratio of the permeance of a gas or a vapor to that of other gas or other vapor. The skin layer is free of defects if the logarithm of permeance is linearly related to the inverse of the measurement temperature. Gas permeation in a non-porous type skin layer on the outer surface as shown in **Fig. 2** is controlled by the solution-diffusion mechanism. Gas and vapor permeation resistance in the porous support layer are significantly small. In addition, practical membranes must have a physical structure and a chemical structure of the thin skin layer and the porous support layer in which the permeation resistance is small in addition to thermal, mechanical, and chemical durabilities depending on the specific application.

4. Application

**Table 3** shows various applications of polyimide hollow fiber membranes.

4.1. N$_2$-enrichment

Some polyimides prepared from BPDA and certain diamines have the characteristic of high permeability. Many applications of N$_2$-enrichment require high
Nitrogen-enriched gas with 90 to 99.9% N₂ concentration conditions are feed pressure of 0.3 to 2.4 MPaG, feed temperature of 0 to 60℃, and concentration of oxygen-enriched gas on the permeate side, because oxygen preferentially permeates through the membrane. Common separation conditions are feed pressure of 0.3 to 10 MPaG and feed temperature of 80 to 140℃.

Blanketing for explosion prevention requires medium purity of 97 to 99% N₂ and tire filling machines require low purity N₂, both at medium flow rates. Polymer membranes for this application are heat resistant up to at least 150℃. Polyimide membranes are resistant to hydrolysis. Polyimides prepared from BPDA and certain diamines are resistant to hydrolysis. Polyimide hollow fiber membranes manufactured from such polyimides have been applied to dehumidification and dehydration processes. The permeance of water vapor is several hundred times greater than that of nitrogen. In general dehumidification applications, compressed air is supplied into the bore-side of the hollow fiber membrane, and nitrogen-enriched gas is obtained on the non-permeate side and oxygen-enriched gas on the permeate side, because oxygen preferentially permeates through the membrane. Common separation conditions are feed pressure of 0.3 to 2.4 MPaG, feed temperature of 0 to 60℃, and concentration of nitrogen-enriched gas with 90 to 99.9% N₂ concentration at flow rate of 0.01 to 1000 Nm³/h.

Analytical equipment and soldering machines require high purity nitrogen gas of 99 to 99.9% N₂ and low flow rate. Laser cutting equipment requires medium purity of 97 to 99% N₂ and tire filling machines require low purity of 95% N₂, both at medium flow rates. Laser cutting equipment requires medium purity of 97 to 99% N₂ for ships and 90 to 95% for oil wells and coal mines, all at high flow rates. The nitrogen-enriched gas also has reduced water vapor and carbon dioxide concentrations, because the permeances of water vapor and carbon dioxide are larger than the permeance of oxygen. Blanketing for explosion prevention on chemical tankers, tire filling machines, analytical equipment, and so on utilize these further purifications.

In contrast, the concentration of oxygen-enriched gas is 25 to 50% O₂ and there are few applications.  

### Table 3: Applications of Polyimide Hollow Fiber Membranes

<table>
<thead>
<tr>
<th></th>
<th>Dehumidification</th>
<th>Dehydration of aqueous organic vapor</th>
<th>Separation of H₂ from hydrocarbons, CO</th>
<th>Separation of CO₂ from hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ generator</td>
<td>Instrument air device</td>
<td>Train brake device</td>
<td>Refining of bioethanol, isopropanol, ketones, etc.</td>
<td>CH₄ and hydrocarbon enrichment from landfill gas, biogas, and natural gas</td>
</tr>
<tr>
<td>Blanketing for explosion</td>
<td>Analytical equipment</td>
<td>Semiconductor manufacturing equipment</td>
<td>H₂ recovery of oil refineries, methanol plants, and ammonia plants</td>
<td></td>
</tr>
<tr>
<td>Laser cutting</td>
<td>Precision equipment</td>
<td>Injection molding</td>
<td>Adjustment of H₂ concentration in chemical plants</td>
<td></td>
</tr>
<tr>
<td>Plastic injection</td>
<td></td>
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<tr>
<td>Food packing</td>
<td></td>
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<tr>
<td>Brewery and beer hall</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Tire filling</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Athlete training</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Soldering for lead-free</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analytical equipment</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OBIGGS (on board inert gas generating system)</td>
<td>Powder storage</td>
<td>Pneumatic transport</td>
<td>(Humidification)</td>
<td></td>
</tr>
</tbody>
</table>

In contrast, there are applications as humidification using the wet side gas obtained on the permeate side.

### 4.3. Dehydration

BPDA-based polyimide hollow fiber membranes with heat resistance have been developed in addition to the features mentioned in section 4.2. for this application. The membranes and membrane module of this application are heat resistant up to at least 150℃. The permeance of water vapor is several hundred times greater than that of ethanol vapor, and is several thousand times greater than that of isopropanol vapor. Common separation conditions that do not condense the water vapor and organic vapors are feed pressure of 0 to 0.2 MPaG and feed temperature of 80 to 140℃.

### 4.4. H₂ Separation

High temperature, high pressure, and long-term use are required for this application. BPDA-based polyimides offer superior heat resistance, mechanical
strength, and durability under unspecified external conditions[38].

The permeance of hydrogen is greater than those of hydrocarbons and carbon monoxide. Hydrogen separation involves many high-pressure conditions. The structure of the membrane module with high-pressure specifications requires that feed gas is supplied into the outer-side of the hollow fiber membrane, and hydrogen-enriched gas is obtained on the bore-side of the membrane.

As an example of hydrogen recovery as part of direct desulfurization in petroleum industry, feed gas containing 92 % H2 is supplied at feed pressure of 13 MPaG, and hydrogen-enriched gas of 99 % H2 at 6 MPaG is obtained. The membranes and membrane modules of this application are pressure-resistant up to at least 15 MPaG. As an example of hydrogen recovery from reformer purge gas, feed gas containing 73 % H2 is supplied at feed flow rate of 30 million Nm3/h, and hydrogen-enriched gas of 99 % H2 is obtained. Operation with high flow rates is possible. In these applications, a two-stage system is often utilized to increase hydrogen recovery. As an example of hydrogen recovery from reformer purge gas, a feed gas of 90 % H2 is supplied at feed temperature of 100 °C, and hydrogen-enriched gas of 98 % H2 is obtained. Polyimide hollow fiber membrane can be also operated at high temperatures.

Three-stage systems may be utilized for high-purity hydrogen production. For example, feed gas of 98.7 % H2 is supplied into the first stage, the permeate gas of hydrogen-enriched gas from the first stage is supplied into the second stage, and the permeate gas of more hydrogen-enriched gas from the second stage is supplied into the third stage. As a result, 99.9996 % H2 is obtained as the permeate gas from the third stage.

4.5. CO2 Removal

The permeance of carbon dioxide is several tens of times greater than that of hydrocarbons. Separation systems to remove carbon dioxide from high-pressure natural gas and to concentrate methane have been widely studied. Requirements for membranes for natural gas purification are similar to requirements for H2 separation, and the design concept is also similar.

Biogas generated from livestock excrement, sewage, and organic waste such as food scraps (biomass) and biomethane recovery from biogas have great potential as renewable energy sources for global environmental protection. Biogas contains about 40 % CO2 and occurs at about atmospheric pressure. Therefore, membranes for biogas applications must operate under relatively low pressure. The biogas is boosted to 0.3 to 1.4 MPaG and supplied into the bore-side of the hollow fiber membrane and methane-enriched gas (biomethane) is obtained on the non-permeate side. The biomethane contains from 90 to 98 % CH4 and methane recovery rate in the range from 70 to 99 %, and industrial plants achieve feed flow rates of several thousand Nm3/h. In countries and regions with strict emission regulations for methane, methane recovery rate is sometimes required to achieve 99 %. In this case, the 2-stage system or 3-stage system is used as the membrane system.

Figure 4 shows the flow patterns of 1-stage and 2-stage membrane systems. Flow patterns B and C describe the 2-stage system, using one and two compressors, respectively. Methane recovery can be increased by the 2-stage system using two compressors as shown in Table 4[38].

5. Conclusion

BPDA-based polyimides offer thermal, mechanical, and chemical durability. In particular, BPDA-polyimides have excellent fiber-forming properties to allow types of hollow fiber membrane which are applicable to industrial gas and vapor separation, and have controlled high-order structures in the membrane. Further applications of polyimide hollow fiber membranes are expected in the future.

References

15) Kasuki, Y., Maka (Membrane), 19, 277 (1994).
A. One Membrane and One Compressor

![Diagram](image1.png)

B. Two Membranes and One Compressor

![Diagram](image2.png)

C. Two Membranes and Two Compressors

![Diagram](image3.png)

Table 4 Compositions and Methane Recovery from Biogas

<table>
<thead>
<tr>
<th>Flow pattern</th>
<th>CH₄ recovery [%]</th>
<th>Composition [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1) Feed</td>
<td>(2) CH₄ rich</td>
</tr>
<tr>
<td>A</td>
<td>76</td>
<td>40.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60.0</td>
</tr>
<tr>
<td>B</td>
<td>81</td>
<td>40.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60.0</td>
</tr>
<tr>
<td>C</td>
<td>97</td>
<td>40.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60.0</td>
</tr>
</tbody>
</table>

要  旨

ポリイミド膜によるガスおよび蒸気分離

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有機系、無機系、金属系材料による分離膜技術が盛んに研究開発されてきており、いくつかの材料が実用化されてきている。種々の酸無水物と多種のジアミンとの組合せから合成されるポリイミドは、系統的な分子設計を検討できる分離膜材料として興味深く検討されてきている。1980年代に石油産業の水素回収に適用されたポリイミド分離膜は、空気分離による窒素富化あるいは酸素富化、除湿、脱水、二酸化炭素分離などのガス分離、および蒸気分離においてその適用範囲をさらに拡大している。3,3',4,4'-ビフェニルテトラカルボン酸二無水物（BPDA）からなるポリイミドは、耐熱性、耐薬品性、機械的強度に優れるとともに、良好な高分子（容易）性を有し、非対称中空糸膜に従来されて、膜分離プロセスとして利用されてきている。ここでは、ポリイミドの材料特性、ポリイミド中空糸膜の特性、ガスおよび蒸気分離の適用場面について紹介する。