

## Development of a multi-layered composite hollow-fiber membrane, MHF

### 1. Introduction

In the field of membrane separation, gas separation technology is used in such applications as hydrogen concentration, gas – liquid gas exchange, and ventilation and deaeration of liquid systems. Because it is produced using a compact, energy-efficient process allowing for continuous operation, it has been the focus of much attention and its market is expanding. The first attempt to separate gases with a membrane was made by Weller and Brubaker in the 1950s when they conducted oxygen concentration from air<sup>1)</sup>. In 1965, an attempt was made to isolate helium with polyethylene hollow fibers. Hollow fibrous membranes for hydrogen separation were first marketed in 1979 under the trade name of prism separators. We focused our attention on previously unknown original gas separation membranes and in 1986 started developing a technology for combining polymer materials with excellent gas permeability performance in an ultrathin membrane. As a result, we developed novel composite hollow fiber membranes with a three-layer structure. They were marketed for the first time in 1992.

### 2. Overview of gas separation technology

The phenomenon of gas permeation in a polymer membrane can be explained by "dissolution and diffusion". Thus, permeation is controlled by adsorption of gas molecules by the membrane and diffusion in the membrane, and the permeation rate  $J$  can be represented by the following formula:

$$J = S \times D \times (p_1 - p_2)/d = P \times (p_1 - p_2)/d \quad (1)$$

where  $S$  is a dissolution coefficient,  $D$  is a diffusion coefficient,  $P$  is a permeation coefficient,  $(p_1 - p_2)$  is a pressure gradient, and  $d$  is the membrane thickness.

The permeation behavior differs depending on whether the polymer membrane is in a rubber-like state or in a glassy state, and several gas permeation models corresponding to those states have been proposed. While we omit the details here, a free volume model proposed for the permeation of gas in a rubber-like polymer membrane agrees well with experimental data, whereas binary adsorption and binary diffusion models of the Henry mode and Langmuir mode are known to explain the permeation behavior in glassy polymer membranes<sup>2)</sup>.

Viewing the relationship between a selective separation coefficient and gas permeation coefficient of a polymer material over a wide region, one can see that there is a tradeoff between the two coefficients, and the separation coefficient of a material with a high permeation coefficient tends to decrease<sup>3)</sup>. Therefore, using a membrane material with a large separation coefficient and making the membrane thickness  $d$  as small as possible are important technological factors in terms of increasing the permeation rate  $J$ , which is a performance characteristic. A variety of methods for reducing the membrane thickness have been heretofore examined and some of them have found practical use. Typical methods for reducing the membrane thickness are shown in Table 1<sup>9)</sup>. However, with all such conventional methods for reducing the membrane thickness, the separation functional layer has a structure exposed on the surface. Therefore, when the membrane is handled or used, there is a very high risk that the thin separation functional layer present on the surface will be damaged and scratches will appear on this surface.

Table 1. Examples of methods of reducing the membrane thickness<sup>9)</sup>

Methods of reducing thickness of composite thin membranes	<ul style="list-style-type: none"><li>• Plasma polymerization method</li><li>• Water surface spread method (LB method)</li><li>• Polymer coating method</li></ul>
Other methods	<ul style="list-style-type: none"><li>• Dry/wet phase conversion method</li><li>• Surface modification method</li></ul>

### 3. Three-layer composite hollow fiber membrane (MHF)

#### 3-1. Specific features of the structure of three-layer composite hollow fiber membrane (MHF)

As described above, within the framework of the conventional technology for producing thin membranes, the method for coating a material with selective gas permeability on the surface of a porous film became predominant. Therefore, when a thin film free of industrial defects was formed, there were limits with respect to film thickness. Another problem was that defects appeared on the surface film during use.

We developed a new composite membrane with the object of overcoming the drawbacks inherent to the conventional systems. The composite membrane has a specific three-layer structure in which a nonporous thin membrane is sandwiched between two porous layers, as shown in Fig.1 and Fig.2. Because the thin membrane functional layer is protected and reinforced, it is protected against damage during use and has a very high reliability. The thin membrane functional layer can be controlled to a very small thickness, and technologically it is possible to obtain a defect-free ultrathin membrane with a thickness at a level of  $0.3 \mu\text{m}$ . With gas permeation performance and compactness of the membrane module as development objectives, the membrane was given a hollow fibrous structure, with an inner diameter of about  $200 \mu\text{m}$ , total membrane thickness about  $25 \mu\text{m}$ , and porosity of the porous layer 40% or more, such a porosity making it possible to ignore the resistance to permeation of gas molecules in the porous support layers<sup>4),5),7)-9)</sup>. As described below, the hollow fiber membrane is formed by integration conducted by a melting method. Therefore, the position of the thin membrane functional layer in the membrane thickness direction can be freely controlled.



Fig.1 Overview of MHF

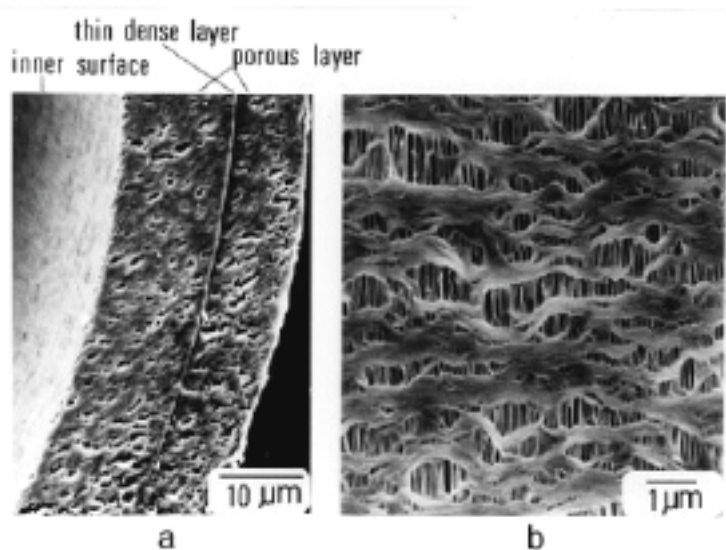


Fig.2 The fine structure of MHF of Cross-section(a) and outside surface(b)

Table 2 shows main physical properties of representative **MHF** in which the thin membrane functional layer is positioned in the intermediate zone in the membrane thickness direction. A thermoplastic polyurethane is used as material for the thin membrane functional layer, and the porous layers serving as support layers are from a highly crystalline polyethylene having excellent mechanical properties.

Table 2 The main physical properties of representative **MHF**

	Unit	<b>MHF</b> – type M
support layers materials	—	high-density polyethylene
thin membrane functional layer materials	—	thermoplastic polyurethane
inner diameter	$\mu\text{m}$	200
membrane thickness	$\mu\text{m}$	40
porosity of the porous layer	%	45
Thickness of thin membrane functional layer	$\mu\text{m}$	0.5
O <sub>2</sub> flux	$\text{cm}^3\text{cm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$	$2 \times 10^{-5}$
O <sub>2</sub> /N <sub>2</sub> separation factor	—	2.7

### 3-2. Specific features of composite formation technology of **MHF**

**MHF** is obtained by sandwiching a thermoplastic polyurethane between high-density polyethylene layers, melt spinning non-stretched hollow fibers with integrated three-layer composite configuration, and then conducting stretching under adequately set conditions. At the stage of non-stretched hollow fibers, the support layer portions composed of the high-density polyethylene are still in a nonporous homogeneous state. The draft ratio, which is the ratio of the linear rate of polyethylene discharge and coiling rate of polyethylene, and cooling conditions of the melt spun polyethylene body are controlled so that the polyethylene layers serving as support layers demonstrate elastic recovery after spinning. In addition, oriented crystallization of polyethylene provides porous polyethylene layers forming the support layers in the subsequent stretching process<sup>10</sup>. On the other hand, the amorphous urethane polymer sandwiched by the polyethylene layers is stretched and reduced in thickness, without becoming porous, in the stretching process. The target hollow fiber membrane with a three-layer composite structure is obtained by thermal setting in the final stage of the process. Thus, the **MHF** production technology is a simple and refined continuous process that can be called a very rational composite forming technology.

Further, because the membrane is manufactured by a method comprising melt spinning and stretching, that is, a method using absolutely no solvent, another specific feature of the process is that it places a very small load on the environment. Moreover, because the film production technology is realized in a clean environment, the **MHF** itself is a membrane with a high degree of clarity.

### 3-3. **MHF** functions, performance and fields of application

Because **MHF** has an excellent gas permeation capability, it functions especially effectively in gas transfer systems of a gas-liquid type. More specifically, it has proven to be suitable for next-generation artificial lungs that are required to demonstrate stable gas exchange performance over a long period<sup>4)-6)</sup>. Porous hollow fiber membranes have been used in conventional lungs. Membranes of this type have excellent gas exchange capability, but they have been shown to have the following drawback. Serum, a blood component, leaked in long-term use. For this reason, in long-term extracorporeal circulation in which the membranes are used for more than several days, for example, as in ECMO (extracorporeal membrane oxygenation), the leak of serum and the resulting decrease of gas exchange performance constituted a serious problem.

In **MHF**, it has been confirmed that due to the presence of non-porous layers in the membrane, serum components do not leak, even in long-term use<sup>6)</sup>. In a gas exchange system of a gas-liquid type, the resistance to gas

permeation is determined by a series resistance comprising the resistance of the membrane itself and the resistance of the boundary film on the liquid side. We have clarified the relationship between the porosity of the porous support layers and the permeation rate of a thin membrane functional layer that allows the resistance of the membrane itself to be ignored, thus designing the membrane structure and performance of the **MHF**<sup>(4,5)</sup>. In long-term extracorporeal circulation testing on goats, it has been confirmed that the membrane is capable of retaining the initial gas exchange performance with good stability over a long period<sup>6)</sup>.

One of the applications of the **MHF** is deaeration conducted to remove gases (oxygen or nitrogen) dissolved in water. Deaeration employs basically the same principle as gas exchange in the above-mentioned artificial lungs and comprises bringing a liquid phase and a gas phase into contact via a membrane and reducing the pressure of the gas phase, thereby transferring and removing the dissolved gas present in water to the gas phase side. An example application is deaeration of ultrapure water in semiconductor production lines. A problem associated with oxygen dissolved in water is that it oxidizes silicon wafers of substrates and forms an oxidation film. In order to resolve this problem, the concentration of dissolved oxygen has to be reduced to an order of ng/L. A compact deaeration module using hollow fiber membrane is optimal for demonstrating deaeration performance at a target level, while maintaining degree of purity of water at an ultrapure level. **MHF** has demonstrated superiority of its gas permeation capabilities also in the field of deaeration and defoaming of test liquids used in the fields of deaeration and inspection devices.

An example of deaeration capability of **MHF** is shown in Fig.3<sup>11)</sup>. In the figure, a low rate (L/min) of water flowing through the **MHF** module is plotted against the abscissa and the concentration of dissolved oxygen (mg/L) in water in the outlet opening of the module is plotted against the ordinate. The numerical value (kPa) units in the figure represent the degree of pressure reduction in the gas phase. As water containing oxygen dissolved to a saturation level is supplied into the hollow fiber membrane of the **MHF** module and moves inside the hollow portions, the oxygen dissolved in the water diffuses and moves to the outside of the membrane under the reduced pressure from the outer side of the membrane and the concentration of dissolved oxygen decreases. The concentration of dissolved oxygen of 8 mg/L in the supplied water can be reduced to an ng/L order by deaeration in the **MHF** module, making it clear that the **MHF** has highly efficient deaeration capability. The **MHF** is suitable not only for deaeration of aqueous systems, but also for various fields of deaeration of nonaqueous solution systems<sup>12)</sup>.

In a gas transfer systems of a gas-liquid type, the gas feed method uses a membrane in a manner opposite that of deaeration. For example, there is a technology for supplying and dissolving carbon dioxide gas in ultrapure water in order to adjust the electric conductivity of the ultrapure water, and the membrane-based gas feed method can be also used in this field.

An artificial carbon dioxide spring device, or balneotherapy device, is an original commercial product of the Mitsubishi Rayon Engineering Co. This is an example of application of the carbon dioxide gas feed system to new commercial products<sup>13)</sup>. This is a device for warm bath therapy in which carbon dioxide is dissolved to a high concentration level in a bubbleless manner in warm water at a temperature of about 40° via an **MHF** module. In the present system, carbon dioxide can be dissolved with a high efficiency to a concentration of 1000 mg/L and higher, and this was found to provide such benefits as improved peripheral blood flow by stimulating blood vessel expansion and pain relief.

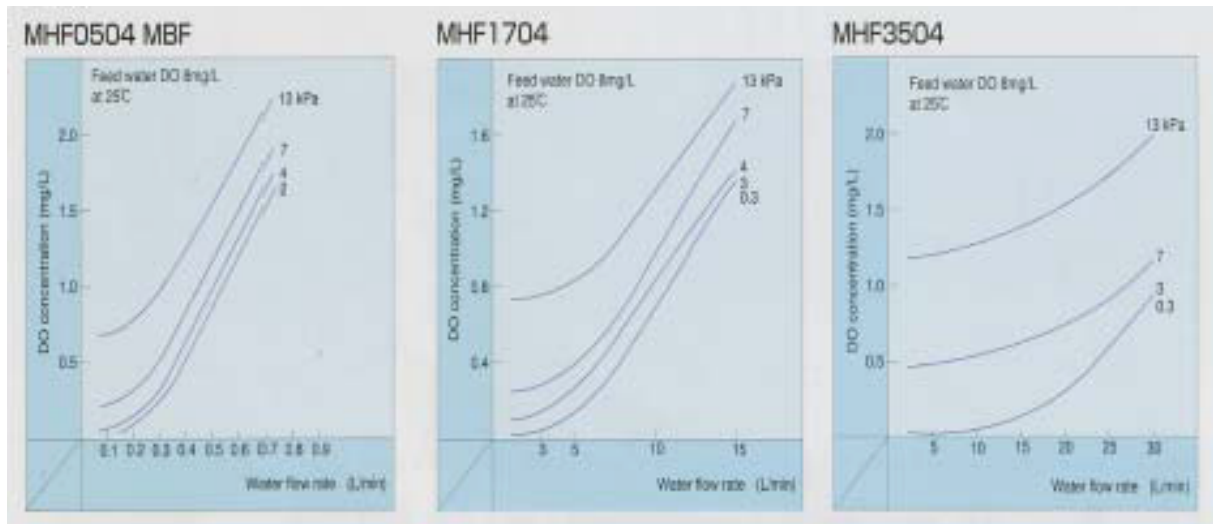


Fig.3 The deaeration capability of dissolved oxygen (mg/L) in water of **MHF** module  
The membrane area of module is starting from the left 0.6m<sup>2</sup>, 15m<sup>2</sup>, 34m<sup>2</sup>

#### 4. Conclusions

The composite hollow fiber membrane **MHF** thus developed has been confirmed to have excellent gas exchange capability as a membrane for next-general artificial lungs and has been found suitable for household and commercial applications, for example, for removing dissolved oxygen from ultrapure water for semiconductor production lines and also deaeration and defoaming various aqueous and nonaqueous liquid systems. Furthermore, as a carbon dioxide feed and dissolution membrane module it is also used in such unique commercial products as an artificial carbon dioxide spring.

Selecting or developing new adequate polymer materials for the functional layer and further improving the technology for the production of thin membranes by melt spinning are expected to expand the applications for the **MHF** gas-liquid systems described in this paper to new fields such as high-performance gas-gas systems (gas separation).

#### Reference

- 1) J.Sakata, Hyomen, 30, 194(1992).
- 2) ex. D. R. Paul and W. J. Koros, J. Polym. Sci. Polym. Phys., Ed., 14, 69(1979).
- 3) ex. L. M. Robeson, J. Membrane Sci., 62, 165(1991).
- 4) J. Kamo, K. Kamada, and T. Takemura, Jinkozoki, 18(N0.2), 1013(1989).
- 5) J. Kamo, M. Uchida, T. Hirai, H. Yoshida, K. Kamada and T. Takemura, Jinkozoki, 14(5), 369(1990).
- 6) E. Tatsumi, Y. Taenaka and H. Akagi, Jinkozoki, 20(No.2), 371(1991).
- 7) M. Uchida, T. Hirai, J. Kamo, H. Yoshida and K. Kamada, 3rd SPSJ International Polymer Conference 42(1990) Preprint.
- 8) J. Kamo, T. Hirai and M. Uchida, senigakai Preprint, 2EO7, F-167(1992).
- 9) J. Kamo, New membrane technology symposium '93, session2, 2-3-1(1993).
- 10) J. Kamo, Senigakai-shi, 49(No.7), P-201(1993).
- 11) The catalogue of **MHF** module of MRC
- 12) M. Uenishi, Maku, 25(No.3), 135(2000).
- 13) M. Uchida, Tansansen, 1(No.1), 17(1998).