

## PREPARATION OF POLYVINYLIDENE FLUORIDE/POLYVINYL DIMETHYLSILOXANE COMPOSITE HOLLOW FIBER MEMBRANES AND THEIR SEPARATION PROPERTIES\*

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**Abstract** Microporous polyvinylidene fluoride (PVDF) hollow fibre membranes were spun using the dry-wet phase inversion method. By means of dip-coating technique, a uniform coating with thickness of around 5–12  $\mu\text{m}$  of polyvinyl dimethylsiloxane (PVDMS) was formed on the surface of porous PVDF hollow fibers. The structural parameters of PVDF substrate membrane were estimated by gas permeation test. Using  $\text{N}_2/\text{O}_2$  as the medium, the separation properties of PVDMS-PVDF composite hollow fiber membranes were also evaluated experimentally. The experimental data of both permeability and selectivity are in good agreement with the theoretical results predicted by the presented pore-distribution model. In order to obtain the compact composite membrane free of defects by the dip-coating technique, the thickness of PVDMS skin must be higher than 5  $\mu\text{m}$ .

**Keywords:** Hollow fiber composite membrane; Gas separation; Dip-coating method

### INTRODUCTION

The issue of volatile organic compound (VOC) emission has captured increasing public and regulatory attention due to its adverse health and environmental impacts. At the moment, two most widely employed emission abatement technologies, *i.e.* carbon adsorption and incineration, are in nowhere fits into the description of a sustainable technology<sup>[1]</sup>. The first involves a transformation of air pollution problem into water pollution during the regeneration of activated carbon, while the latter aims at the destruction of contaminated stream with the addition of fuel. Furthermore, from economic point of view, none of them present any attractive monetary revenue. Membrane-based vapour permeation technology, on the other hand, is capable of tackling these two key issues together as it allows the valuable compounds to be recaptured in a reusable manner, left behind minor contaminated stream well below the regulatory allowable level<sup>[2, 3]</sup>. To date, most works reported on vapour permeation applications have been focused intensely on polymeric composite membranes whereby a glassy polymer was incorporated into microporous substrates and coated with silicone rubber, *i.e.* polydimethylsiloxane (PDMS). The glassy polymer, known for its high gas permeability, however, is not the ideal selection for vapour permeation as it is not vapour selective. Rubbery polymer, *i.e.* PDMS, is undoubtedly known for its good selectivity but is difficult to stand alone and handle due to its sticky nature. A combination of the two allows the membrane properties to be tailored to vapour permeation. Although the porous substrate layer is good only for mechanical support but not to impair the intrinsic separation property of the selective coating layer, it still influences the overall membrane transport and separation performance<sup>[4, 5]</sup>.

Among the commonly used support membranes include polysulfones (PSF), polyethersulfone (PESF), polyimide (PI), polyamide (PA) and Celgard (Polypropylene) membranes. In recent years, polyvinylidene fluoride

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(PVDF) became a novel membrane material since it is hydrophobic in nature and can be used to fabricate asymmetric membrane using the phase inversion method, and the hollow fibre membrane thereof was found to favour water permeation and proven to have intrinsically organic selective property<sup>[6]</sup>. Regardless of the microporous support membrane used, so far silicone rubber is still the most widely used coating material in vapour permeation studies. Silicone rubber, in general, possesses high thermal stability because of the high bond energy of its main structure, and also, it can be easily fabricated into ultra thin film. However, conventional silicone rubber is found to be rather susceptible to gasoline vapour attack therefore it is not expected to be a good choice for the recovery of  $C_6 - C_8$  hydrocarbons, which are the main components of gasoline<sup>[7, 8]</sup>. Moreover, silicones are known to swell due to vapours sorption, leading to a lower transport resistance for any species diffusing through the swollen polymer and the loss of selectivity. Lots of efforts have been channeled into the synthesis and modification of silicone rubber coupled with the search for alternative polymeric materials capable of recovering VOC from either gas or liquid streams with better selectivity, higher permeability as well as greater durability<sup>[9, 10]</sup>. Polyvinyl dimethylsiloxane (PVDMS) was proven to be free of those drawbacks for the conventional silicon rubber<sup>[11]</sup>.

In this work, PVDMS-PVDF composite hollow fiber membranes were prepared by the dry-wet phase inversion method and followed with the dip-coating technique. The thickness of coated films was controlled by modulating the coating solution concentrations. The separation properties of such prepared membranes were evaluated using  $N_2/O_2$  mixture as the separation medium.

## EXPERIMENTAL

### Materials

Porous PVDF hollow fiber membranes were prepared by using the dry-wet phase inversion method as detailed by Wang *et al.*<sup>[12]</sup>. To prepare the polymer dope, *N,N*-dimethylacetamide (DMAc) [99.9+%, HPLC, Sigma Aldrich] was used as the solvent and glycerol [ $F_w = 92.09$ , 99%], lithium perchlorate ( $LiClO_4$ ) [99+%, ACS] and polyvinylpyrrolidone (PVP) [99.9+%,  $M_w = 1 \times 10^4$ ] as additives. Water was used as the coagulant to prepare the PVDF hollow fibres.

### Fabrication of Porous PVDF Hollow Fiber Membranes

Different compositions of clear and homogeneous polymer dopes consisting of PVDF, DMAc, and additives were prepared as reported by Wang *et al.*<sup>[12]</sup>. Then the polymer dope was transferred to a stainless steel reservoir and pressurized to 20–30 psig using  $N_2$ . The spinneret with an orifice diameter of 0.42 mm and an inner tube diameter of 0.30 mm was used to obtain PVDF hollow fibres. The fibres were spun by the wet process (air-gap = 0) at room temperature. The spinning rate is fixed at 1.2–1.5 m/min and the temperature of coagulation bath is 50°C. The prepared hollow fibres were immersed in fresh water for at least 7 days to complete solidification process and then examined their properties.

### Coating of the PVDF Hollow Fiber Membranes

The coating solution was prepared by dissolution of PVDMS (United Chemical Technologies, Inc.) in hexane where the concentration of PVDMS was changed in the range of 5–12% in weight. To coat the PVDF hollow fibers, they were firstly cut and assembled into bundle with a length of 10–15 cm. In the pre-treatment step, the hollow fiber bundle was immersed in hexane solution for 1 min at ambient condition (25°C, 60% RH), followed by heat treatment at 50°C for 4 h. After that, the treated hollow fibers were allowed to cool to room temperature, followed by dip-coating whereby it was immersed in the coating solution with vacuum pressure applied at the fiber's lumen side for an intended duration, generally 2 min. This was followed by post-treatment at 50°C for 24 h. The thickness of the coated film was examined using a scanning electron microscopy (SEM) (Hitachi S-4100). The morphology of the original PVDF hollow fiber membrane and the coated membrane is shown in Fig. 1 (a) and (b), respectively. As can be seen, the thickness of the coated PVDMS layer is very uniform and the interface between the original PVDF and the coated layer is very compact.

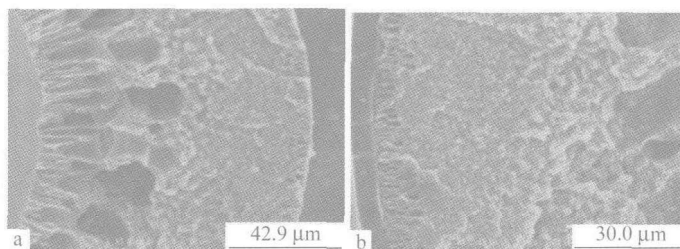


**Fig. 1** Scanning electronic micrographs of the hollow fiber membranes  
a) Original PVDF; b) Coated PVDMS/PVDF composite membrane

### Gas Permeation and Separation Test

The structural parameters of the porous hollow fiber membranes were determined by the gas permeation test. In order to measure the permeability of the membrane, a module containing 2–5 fibers was made. The upstream pressure was in the range of 5 to 30 psi (Pa), which was measured by a pressure transducer (Basingstoke, England). Nitrogen gas was used as a standard gas and the permeation flux was measured at  $(25 \pm 1)^\circ\text{C}$  and atmospheric pressure using a soap-bubble flow meter. The parameters including effective surface porosity, mean pore radius and standard deviation of pore size were determined by regressing the experimental data.

The separation performance of the coated composite membranes was tested and evaluated in a  $\text{N}_2\text{--O}_2$  separation system. A module containing 5–10 coated hollow fibers was used and was housed in a constant temperature box. A air gas was fed into the shell side of the hollow fiber membrane module. Perkin Elmer 8700 gas chromatograph was used to analyse the compositions of the permeated and the residue gases with a TCD detector. The flow rate of the gases was measured at room temperature and atmospheric pressure using a soap-bubble flow meter.

## THEORY

### Mass Transport Through Asymmetric Porous Membranes

For a good asymmetric membrane, the porous supporting layer should provide negligible resistance and the gas permeation is mainly determined by the skin layer. The total gas permeation may be the combination of those through the membrane pores and the nonporous medium of the skin layer. Therefore, the total gas permeation rate through the asymmetric membrane can be written in a general non-mechanistic flux equation as

$$N = P_1 A_t \Delta p = P_p A_p \frac{\Delta p}{L_p} + P_s A_s \frac{\Delta p}{L_s} \quad (1)$$

where  $N$  is the total permeation rate ( $\text{mol} \cdot \text{s}^{-1}$ ),  $A_t$ ,  $A_p$  and  $A_s$  are the total membrane permeation area, porous area and nonporous area on the membrane surface ( $\text{m}^2$ ), respectively;  $L_p$  and  $L_s$  are the effective pore length and effective skin layer thickness (m), respectively,  $P_p$  and  $P_s$  are the permeability coefficients of gas transport in the pores and the nonporous medium of skin layer ( $\text{mol m} \cdot \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ), respectively, and  $\Delta p$  is the pressure differential across the membrane (Pa). This equation is derived on the assumption of uniform pore length and uniform thickness of the skin layer. Obviously, the gas permeation coefficient through the porous membrane substrate,  $P_1$  is given by

$$P_1 = P_p \frac{\varepsilon}{L_p} + P_s \frac{1-\varepsilon}{L_s} \quad (2)$$

where  $\varepsilon$  is the surface porosity of the skin layer that is defined by

$$\varepsilon = \frac{A_p}{A_t} \quad (3)$$

The permeability coefficient through nonporous medium of membrane skin layer can be described in terms of solution-diffusion mechanism, which is expressed by

$$P_s = P_s^0 \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where  $P_s^0$  is the pre-exponential factor ( $\text{mol m} \cdot \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ) and  $E_a$  is the activation energy of gas permeation ( $\text{J} \cdot \text{mol}^{-1}$ ).

On the other hand, the permeation through membrane pores is the result of different transport mechanisms, *i.e.*, Knudsen diffusion, slip flow, viscous flow (Poiseuille flow) and surface flow, depending on the membrane structure and the operating condition<sup>[13]</sup>. However, the surface flow can also be neglected at a lower pressure<sup>[12]</sup>, and thus will not be taken into consideration in this work. When a gas transports through a long capillary pore of a membrane with the radius of  $r$  by Knudsen flow, slip flow and viscous flow, their molar flux can be expressed in the following three equations respectively

$$J_K = \frac{2}{3} \left( \frac{8}{\pi MRT} \right)^{0.5} r \frac{\Delta p}{L_p} \quad (5a)$$

$$J_s = \left( \frac{\pi}{8 MRT} \right)^{0.5} r \frac{\Delta p}{L_p} \quad (5b)$$

$$J_v = \frac{r^2}{8\mu RT} \bar{p} \frac{\Delta p}{L_p} \quad (5c)$$

where  $J_K$ ,  $J_s$  and  $J_v$  are the gas molar flux ( $\text{mol} \cdot \text{m}^{-2} \text{s}^{-1}$ ) under Knudsen flow, slip flow or viscous flow, respectively.  $R$  is the gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$ ),  $M$  is the molecular weight ( $\text{kg} \cdot \text{mol}^{-1}$ ),  $\mu$  is the viscosity of gas ( $\text{Pa} \cdot \text{s}$ ),  $T$  is the operating temperature (K) and  $\bar{p}$  is the mean pressure across the membrane (Pa). The specific transport mechanism in the pores depends on the ratio of pore radius to the mean free path of permeate gas  $\lambda$ , which is expressed as:

$$\lambda = \frac{RT}{\sqrt{2\pi} d^2 N \bar{p}} \quad (6)$$

where  $d$  is the diameter of gas molecule (m), and  $N$  is the Avogadro number.

A typical discrimination criterion for these transport mechanisms is as follows: when  $r/\lambda \leq 0.05$ , Knudsen flow would predominate the permeation; slip flow would predominate the permeation in the section of  $0.05 < r/\lambda \leq 3$ ; and viscous flow is the predominant factor when  $r/\lambda > 3$ .

However, it should be recognised that it is almost impossible to obtain pores with one uniform diameter in membranes prepared by the phase inversion method, but rather a distribution of pore sizes<sup>[2]</sup>. It is therefore rational to take the membrane pore size distribution into consideration. The log-normal distribution functions was usually used to describe the pore distribution of asymmetric membranes<sup>[14]</sup>, that is,

$$g(r) = \frac{1}{\sqrt{2\pi} r} [\ln(1 + \sigma^2)]^{-0.5} \times \exp\left[-\frac{(\ln(r/r_m)(1 + \sigma^2)^{0.5})^2}{2 \ln(1 + \sigma^2)}\right] \quad (7)$$

where,  $r_m$  is the mean pore radius, m; and  $\sigma$  is the dimensionless standard deviation of the membrane pore size. They can be determined independently by regressing the permeability with experimental data for gas permeation test<sup>[13]</sup>.

As a result, the gas permeability through membrane pores  $P_p$ , may be then given by

$$P_p = \frac{C_1 \int_0^{0.05} r^3 g(r) dr + C_2 \int_{0.05}^3 r^3 g(r) dr + C_3 \int_3^{r_{\max}} r^4 g(r) dr}{\int_0^{r_{\max}} r^2 g(r) dr} \quad (8)$$

where

$$C_1 = \frac{2}{3} \left( \frac{8}{\pi MRT} \right)^{0.5}, \quad C_2 = \left( \frac{\pi}{8 MRT} \right)^{0.5}, \quad C_3 = \frac{\bar{p}}{8\mu R} \quad (8a)$$

Substituting (4) and (8) into Eq. (2) gives the substrate permeability for gas as

$$P_1 = \frac{1-\varepsilon}{L_s} \cdot P_s^0 \exp\left(-\frac{E_a}{RT}\right) + \frac{\varepsilon}{L_p} \cdot \frac{C_1 \int_0^{0.05r} r^3 g(r) dr + C_2 \int_{0.05r}^{3r} r^3 g(r) dr + C_3 \int_{3r}^{r_{\max}} r^4 g(r) dr}{\int_0^{r_{\max}} r^2 g(r) dr} \quad (9)$$

### Mass Transfer in the Coated Membrane

As it is well known to all, the resistance to gas transport mainly exists within the coated skin and the gas film resistance is generally negligible. As a result, the flux of gas permeating through a coated membrane may be written as:

$$J = P_1(p_u - p_s) = \frac{P_2}{\delta}(p_s - p_d) \quad (10)$$

where  $P_2$  is gas permeability through the coated skin,  $\text{mol m}^{-1} \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ;  $\delta$  is the skin thickness, m;  $p$  is the gas pressure Pa; and the subscripts  $u$ ,  $s$ ,  $d$  represent upstream, interface between the substrate and skin and downstream respectively. The total gas permeation coefficient is therefore given by

$$P_t = \frac{1}{1/P_1 + \delta/P_2} \quad (11)$$

The permselectivity of the coated membrane is generally defined as the ratio of permeabilities for two gases:

$$\alpha_{A/B} = \frac{P_{t,A}}{P_{t,B}} \quad (12)$$

## RESULTS AND DISCUSSION

In this section, the effects of porous substrate and coated film on the separation performance of composite membranes were firstly studied theoretically. Since the oxygen and nitrogen permeability values of PVDMS are unknown, the corresponding values of the conventional silicon rubber, which are  $2.143 \times 10^{-13}$  and  $9.376 \times 10^{-14} \text{ mol m}^{-1} \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$  for oxygen and nitrogen respectively, were used. Further, the experimental results of the separation properties of PVDMS-PVDF composite hollow fiber membranes are given and analyzed with the presented mathematical model

### Effect of Coating Thickness

As it is known to all, the coated film increases the resistance of composite membrane to gas transport with the result of decrease in gas permeability. Figure 2 shows the effect of coating thickness on the oxygen permeability at different effective porosity of substrate where the mean pore size and standard deviation are kept constant. In this figure oxygen permeability through the pure silicon rubber is also plotted against the coating thickness, which is illustrated as a dotted line. It can be seen that the thinner the coated film, the more remarkable is the effect of porous substrate on the gas permeability. In the meantime, as the coating is thicker than  $8 \mu\text{m}$ , which is usually true in most practical uses, oxygen permeability of the composite membrane is close to the maximum value that is shown as the dashed line when the effective porosity of substrate is up to  $50 \text{ m}^{-1}$ . Therefore, it may be concluded that the resistance of substrate to gas permeation can be neglected if the effective porosity is higher than  $50 \text{ m}^{-1}$ , at which the gas permeability attains  $2.2 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ .

The relationship between the selectivity of oxygen/nitrogen and the coating thickness is shown in Fig. 3. It may be seen that the selectivity increases with the thickness of coated skin, and gradually approaches to the maximum value that is for the pure silicon rubber as the coated skin becomes thicker and thicker. In the meantime, the membrane selectivity also increases as the effective porosity of substrate is increased even if the coating thickness is kept the same. In other word, it is also possible to achieve a high selectivity for a thin coating skin only if the resistance of substrate is kept very low. For example, for a substrate with an effective porosity of  $1000 \text{ m}^{-1}$ , the permeability of which is  $4.86 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ,  $2 \mu\text{m}$  of coating thickness is enough to achieve the highest selectivity. Conclusively, it is recommended to decrease the resistance of substrate

rather than to increase the coating thickness in order to achieve a high selectivity because a higher coating thickness would simultaneously result in a sharp decrease in gas permeability, just as discussed above. Of course, the thinner coated skin would more possibly lead to the formation of defects.

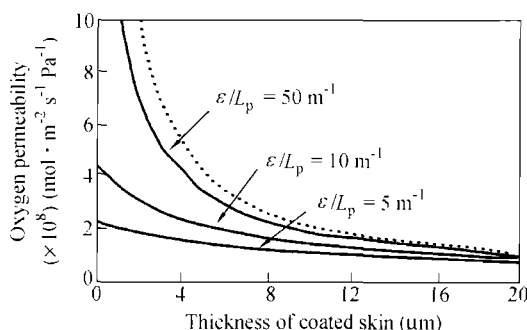


**Fig. 2** Effect of coating thickness on the oxygen permeability at 298 K ( $r_m = 0.05 \mu\text{m}$ ,  $\sigma = 0.4$ )

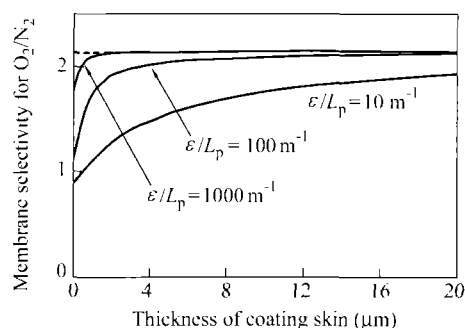


**Fig. 3** Effect of coating thickness on the permselectivity of oxygen/nitrogen at 298 K ( $r_m = 0.05 \mu\text{m}$ ,  $\sigma = 0.4$ )

### Effect of Porous Substrate

The effect of porous substrate structure on the permeability and selectivity is illustrated in Fig. 4. As expected, the membrane permeability for gases increases with the increase of both mean pore radius and standard deviation since the substrate resistance to mass transfer is reduced. However, if the mean pore radius is too small, gas permeability cannot attain to the maximum value (for pure silicon rubber) even if the standard deviation is very high. Meanwhile, it may also be seen that both the permeability and selectivity are hardly changed at either very high or very low standard deviation values, which means that the gas permeation process is primarily controlled by the coated layer. As we know, the lower value of standard deviation is always desired for a readily coated film. Therefore, the porous substrate for coating should possess a suitable mean pore radius (not too small) with the uniform pore size. Such structure is also essential to promoting the selectivity of composite membranes, as shown in this figure.

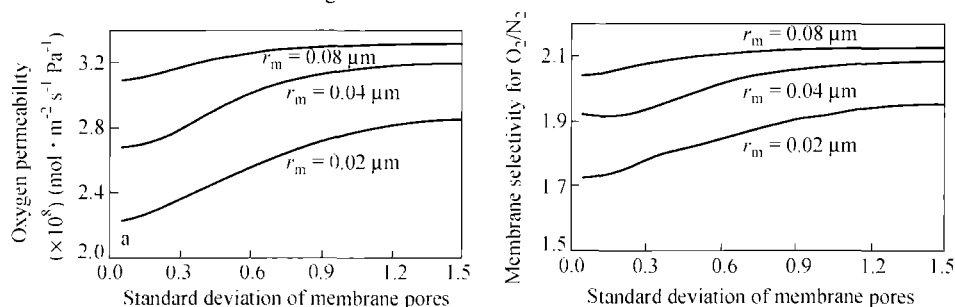


**Fig. 4** Effect of porous substrate on gas permeability ( $\varepsilon/L_p = 50 \text{ m}^{-1}$ ,  $\delta = 6 \mu\text{m}$ ,  $T = 298 \text{ K}$ ,  $p_u = 0.5 \text{ MPa}$ )

### Effect of Operating Pressure

Figure 5 shows the effect of operating pressure (upstream) on the gas permeation of membranes with different structure. Since the mean free path of permeate gas changes with operating pressure, its effect on gas permeation is very complicated. As can be seen from the figure, when the mean pore size of membrane is  $0.02 \mu\text{m}$ , the oxygen permeability is slightly decreased with increasing the operating pressure at lower pressure values and then slightly increased at higher pressure. However, because the nitrogen permeability is hardly changed as operating pressure increases (in fact it is increased in a very small degree), the selectivity for  $\text{O}_2/\text{N}_2$  has the same trend as the oxygen permeability. As the mean pore radius increases to  $0.04 \mu\text{m}$ , both oxygen permeability and membrane selectivity for  $\text{O}_2/\text{N}_2$  become more sensitive to the operating pressure, which implies that the substrate plays an important role in the gas permeation process. If the mean radius of membrane pores is further

increased to  $0.1\ \mu\text{m}$ , the gas permeability and membrane selectivity increase with the operating pressure in the whole range. Moreover, the gas permeability and selectivity for such membrane are less dependent on the operating pressure compared with the smaller pores. This is because the coated skin gradually plays much a role in the gas permeation as the operating pressure increases. Obviously, it may be expected that the gas permeation through membranes with a thickly coated film is nearly independent of the operating pressure, just as shown in the same figure as dotted lines. Conclusively, the high operating pressure favors the gas permeation through the membranes with substrate of large pores but is not desired for those with substrate of small pores.

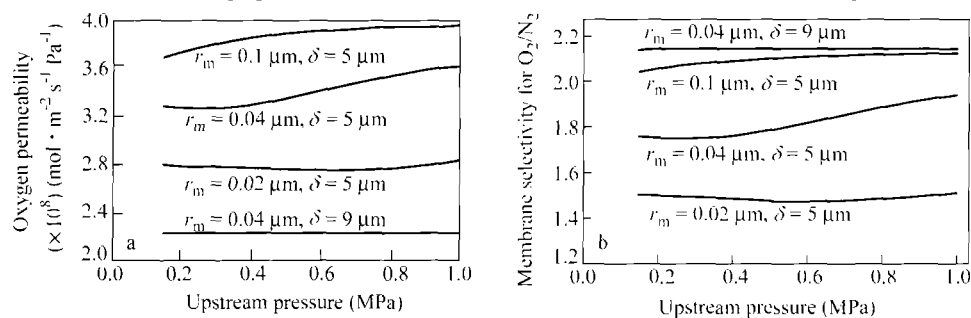


Fig. 5 Effect of operating pressure on gas permeation ( $\varepsilon/L_p = 50\ \text{m}^{-1}$ ,  $\sigma = 0.4$ ,  $T = 298\ \text{K}$ )

### Experimental Results

The permeability of PVDF hollow fiber membrane substrate was measured as shown in Fig. 6. By regressing the experimental permeability data with the pore-distribution model, the microstructure parameters of PVDF membrane may be obtained as follows: effective porosity =  $26\ \text{m}^{-1}$ , mean pore radius =  $2.1 \times 10^{-8}\ \text{m}$ , and standard deviation of pore size =  $0.12$ . It can be seen that the experimental permeability data for porous membrane can be satisfactorily predicted with the present pore-distribution model.

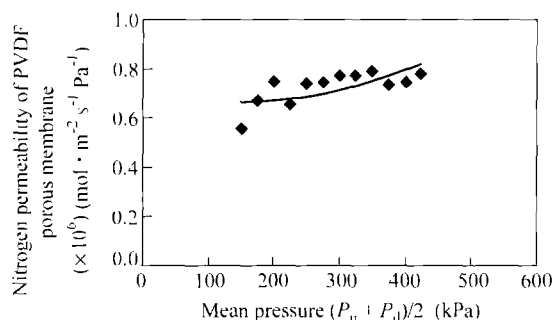


Fig. 6 Plot of nitrogen permeability of PVDF porous membrane against the mean pressure

Figure 7 shows the permeability of the PVDMS-PVDF composite membrane for oxygen and nitrogen, which were measured at  $298\ \text{K}$  and the upstream and downstream pressures were  $203$  and  $101\ \text{kPa}$ , respectively. The permeability coefficients of the PVDMS material used in calculation were, respectively,  $1.41 \times 10^{-13}$  and  $5.813 \times 10^{-14}\ \text{mol} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  for oxygen and nitrogen, which were obtained by means of regressing the experimental data. It may be seen that the calculated values of permeability are in good agreement with the experimental data after the coating thickness of PVDMS skin is thicker than  $5\ \mu\text{m}$ . The reason why the experimental data of permeability are much higher than the predicted values for thinner coating is that some defects may possibly exist within the PVDMS skin. As a result, the permselectivity for  $\text{O}_2/\text{N}_2$  is lower than the theoretical results, as shown in Fig. 8. It demonstrates that PVDMS skin with at least  $5\ \mu\text{m}$  thickness must be coated in order to obtain a compact composite membrane free of defects. In addition, the experimental results also indicate that the permselectivity of PVDMS for oxygen/nitrogen is somewhat higher than the conventional silicone rubber, i.e.  $\alpha_{\text{O}_2/\text{N}_2} = 2.43$ .

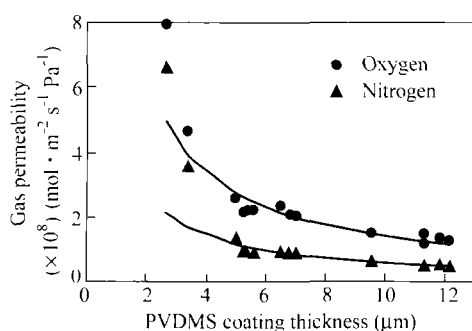


**Fig. 7** Permeability of the PVDMS-PVDF composite membrane at 298 K ( $p_u = 203$  kPa,  $p_d = 101$  kPa)

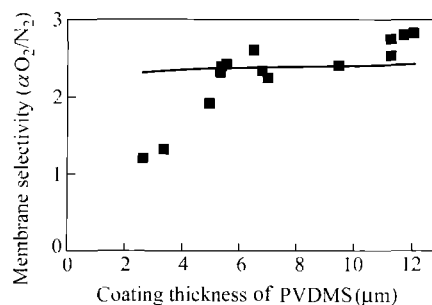


**Fig. 8** Selectivity of the PVDMS-PVDF composite membrane for oxygen and nitrogen separation

## CONCLUSIONS

The structure of porous substrate influences remarkably the gas permeability of composite membranes. The porous substrate membrane for coating should possess a suitable mean pore radius (not too small) with uniform pore size.

It is more effective to decrease the resistance of substrate than to increase the coating thickness so as to promote the selectivity of composite membrane. In addition, it is possible to achieve both high selectivity and permeation flux by using a substrate with little resistance and a thin skin coating.

The operating pressure depends on the porous substrate; high operating pressure favors the gas permeation, through the membranes with substrate of large pores but is not desired for those with small pores.

The experimental data of the PFDMS-PVDF hollow fibre composite membranes for gas separation may be predicted perfectly by the present pore-distribution model. In order to obtain a compact composite membrane free of defects by dip coating technique, the PVDMS skin must be thicker than 5  $\mu\text{m}$ .

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