Effect of support layer on gas permeation properties of composite polymeric membranes

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Abstract−PES/Pebax and PEI/Pebax composite membranes were prepared by coating the porous PES and PEI substrate membranes with Pebax-1657. The morphology and performance of the prepared membranes were investigated by SEM and CO_2 and CH_4 permeation tests. The CO_2 permeances of 28 and 52 GPU were achieved for PES/Pebax and PEI/Pebax composite membranes, respectively, with CO_2/CH_4 selectivities almost equal to that of Pebax (26). The experimental data were further subjected to a theoretical analysis using the resistance model. It was found that the porosity and the thickness of the dense section of PES substrate were an order of magnitude higher than those of PEI substitute. The porosity/thickness ratio of PEI substrate was, however, higher than PES, explaining the higher permeance of PEI/Pebax composite membrane. Substrates with porosities much higher than the Henis-Tripodi gas separation membrane were used in this work, aiming to achieve the selectivity of Pebax, rather than those of the substrate membrane materials.

Keywords: PES/Pebax, PEI/Pebax, Gas Permeation, Permeability, Substrate Effect

INTRODUCTION

CO_2 separation from a mixture of light gases, such as CH_4, O_2, N_2 and H_2, by synthetic membranes is one of the rapidly growing fields of industrial importance due to the advantages of membrane separation processes such as small footprint, high energy efficiency and environmental sustainability. The technology seems especially effective for the CO_2 capture from combustion flue gas [1-4].

Many different materials have been used for gas separation membranes including both organic (polymers) and inorganic (ceramic, glass, metals, carbon molecular sieve and clay) [2,5,6]. Polymeric membranes are, however, commercially dominant due to their flexibility, processability and low price. Among the polymeric materials, membranes made of glassy polymers can exhibit high selectivity, which is the main reason why they are preferred to rubbery polymers [7]. But their permeability is low and they are susceptible to performance deterioration over time caused by either polymer densification or plasticization [7,8]. The performance of membrane materials generally falls within the trade-off relationship between permeability and selectivity, as shown by Robeson [9]. Many attempts have been recorded in the literature to surpass Robson's upper line by designing the chemical structure of the polymer including the polymer blend.

Lin and Freeman [10] made an overview about membrane material selection for CO_2 removal from the gas mixtures. The presence of polar ethylene oxide (EO) subunits in the polymer backbone increases the dipole-dipole interactions with CO_2 and consequently increases CO_2 permeability (P_{CO_2}), which leads to the enhancement of its selectivity over other light gases such as CH_4 (P_{CO_2}/P_{CH_4}) [11]. However, in the homo-polymer, EO tends to crystallize at high pressures, decreasing gas permeability substantially.

In recent years, a large number of studies have focused on development of PEO-based membranes for gas separation. These studies have eventuated in different grades of Pebax such as 1074, 1657, 2533 and 3533 [12-22]. These copolymers have been used as pure or mixed with other ingredients for membrane gas separation applications [23-25]. The gas transport in Pebax membranes depends not only on the fractions and the nature of the constituting chemical blocks (i.e., the polar group content), but also on the length of the blocks [26]. All these parameters are likely to control the phase structure and properties, such as the compactness (i.e., free volume) of the permeating phase and the detailed organization of the polymer segments in this phase that governs the gas mobility. The polyamide crystalline phase affects these structural properties and thus the gas permeability, via its interfacial actions on the polymer segment in the vicinity of the phase interface and its distribution in the membrane. The Pebax-1657 grade offered the best compromise in different structural factors for CO_2 removal [26,27]. Pebax-1657 is a rubbery copolymer that consists of 60 wt% PEO and 40 wt% polyamide, wherein PEO segments act as permeable phase and the polyamide crystalline phase gives the mechanical strength to the membrane. The chemical structure of Pebax-1657 is shown in Fig. 1 [28].

Although Robson's upper line offers an excellent guideline for the choice of membrane material with high selectivity and perme-

$$HO-(C_2H_4O)_x \left[\begin{matrix} O \\ \| \\ (C-C_5H_{10}-NH)_y \end{matrix} - \begin{matrix} O \\ \| \\ C \end{matrix} - C_2H_4 - \begin{matrix} O \\ \| \\ C \end{matrix} -(OC_2H_4)_x \right]_n OH$$
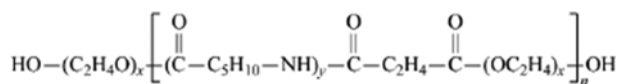
Fig. 1. Chemical structure of Pebax-1657.

ability, a practical membrane with high permeance without compromising the selectivity can only be fabricated by making the selective polymer layer as thin as possible. The composite membrane in which a thin selective layer is coated on top of a porous support may achieve this goal.

In general, membranes applied in pervaporation, reverse osmosis (RO), forward osmosis (FO) and sometimes in gas separation are composite membranes. By this method, the membrane thickness is reduced without adversely affecting the mechanical strength of the membrane [29]. The gas separation performance of the composite membrane depends on several factors, including the properties of the top layer and the porous support [30], as well as the methods and conditions of coating. The supporting materials should be porous enough to avoid additional mass transfer resistance against the permeating compounds [31], while the selective layer has a crucial role in determining the permeation characteristics of the membrane [32]. Casting and dip coating of PDMS on a porous PES substrate were compared by Madaeni et al. [31], who concluded that the thickness of PDMS layer as well as the membrane permeance depend on the coating method. By casting, PDMS solution penetrates more into the substrate pores, increasing the gas transport path length.

Jadav et al. [32] also studied the coating of polydimethyl siloxane (PDMS) layer on the porous polysulfone substrate and reported that the difference between the experimentally observed and the theoretically calculated thickness of the coated layer was caused by the penetration of the PDMS solution into the pores of the polysulfone (PSf) substrate. The lower the PDMS concentration in the coating solution, the more solution penetration took place.

Understanding how composite membrane structural characteristics influence the performance of the membranes is crucial to further development of this membranes. Sublayer structural characteristics such as surface porosity, pore size and porosity/thickness ratio are also important parameters that affect composite membrane performance. Many studies have been done to investigate the effect of support layer on composite membrane performance in pervaporation [33], nanofiltration [34,35], forward osmosis [36, 37] and gas separation [30,38] applications.

Zhu et al. [30] applied computational fluid dynamics (CFD) simulation to study the effect of support layer structure on gas separation performance of polycarbonate/Teflon Af1600 gas separation membrane. They concluded that porosity, pore size and pore dispersion of the support layer affect membrane performance. Their experimental and simulation results showed that high flux composite membranes require high porosity and small pores with regular arrangement in support.

Wijmans et al. [38] also used simulations based on CFD to quantify the restrictive influence of a porous support on molecular diffusion in the top layer because the molecules can exit the top layer only when a pore exists underneath. Until the gas molecule arrives the pore it has to pass through a longer distance in the coated layer. CFD simulations were also performed for composite membranes containing a gutter layer, showing that a gutter layer with high permeability can significantly improve the permeance.

Chung et al. [39] determined the permeability of the thin layer coated on top of a microporous support using a resistance model. Chung's group prepared two- and three-layer composite membranes of polyvinyl pyrrolidone (PVP)/PSf and PDMS/PVP/PSf to determine PVP permeability and selectivity for CO_2 and CH_4 gases.

In the present study, Pebax-1657 dense films, PES/Pebax-1657 and PEI/Pebax-1657 composite membranes were prepared to investigate the gas separation performance of the composite membranes. Particularly, the effects of the selective top layer thickness and the substrate on the gas transport properties of the composite membranes were evaluated. The experimental data were further analyzed by using the resistance model to know more about the detailed structures of the composite membranes and their effects on the membrane performance.

THEORY

The resistance model assumes that the composite membrane consists of several barrier layers stacked together in series. There is a clear discontinuity at the boundary of two neighboring barrier layers, either in chemical structure or morphology [40].

Henis and Tripodi [41] developed composite membranes for gas separation based on the series resistance model as a theoretical guiding principle. According to the model, the total resistance of a composite membrane is calculated on the following assumptions:

• Gas flow through membrane is one dimensional
• The dense section of asymmetric substrate layer has uniform thickness
• Intrusion depth of top layer is equal to that of dense layer of the substrate
• The defects on the top layer coating are negligible.

In the model, the resistance, R (1/GPU), for gas transfer is given by:

$$R = \frac{1}{(P/l)} \tag{1}$$

where P is permeability (Barrer$=10^{-10}$ cm^3 (STP) cm/cm^2 s cmHg) and l is thickness (μm). (P/l) is called permeance and its dimension is GPU (1 GPU$=10^{-6}$ cm^3 (STP)/cm^2 s cmHg).

According to the resistance model, the composite membrane consists of the resistances from the three layers as shown in Fig. 2.
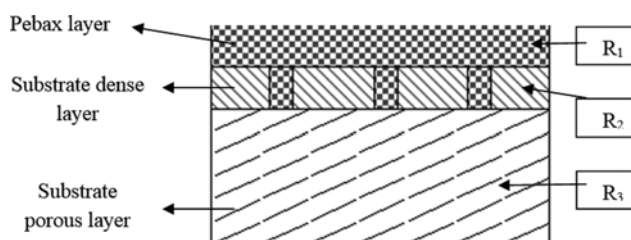

Fig. 2. Three resistances in composite membranes.

R_1 is the resistance of the top Pebax layer, R_2 is the resistance of the intermediate layer, where the pores of the dense section of the substrate membrane (either polyethersulfone (PES) or polyetherimide (PEI)) are filled with Pebax and R_3 is the resistance of the macroporous layer underneath. Assuming R_3 is negligible compared to R_1 and R_2, the total resistance, R_t, is given by:

$$R_t = R_1 + R_2 \qquad (2)$$

From Eq. (1)

$$R_t = \frac{1}{(P/l)_{total}} \qquad (3)$$

Where $(P/l)_{total}$ is the total permeance of the composite membrane and

$$R_1 = \frac{1}{(P/l)_{Pebax}} = \frac{1}{P_{Pebax}} \qquad (4)$$

where l_1 is the thickness of the top Pebax layer and P_{Pebax} is the permeability of Pebax.

From Eqs. (2), (3) and (4)

$$R_2 = \frac{1}{(P/l)_2} = \left\{ \frac{1}{(P/l)_{total}} - \frac{l_1}{P_{Pebax}} \right\} \qquad (5)$$

Then the CO_2/CH_4 selectivity of the intermediate layer is given by

$$\alpha_{2,\,CO_2/CH_4} = \frac{(P/l)_{2,\,CO_2}}{(P/l)_{2,\,CH_4}} = \frac{\left\{ \dfrac{1}{(P/l)_{total,\,CH_4}} - \dfrac{l_1}{P_{Pebax,\,CH_4}} \right\}}{\left\{ \dfrac{1}{(P/l)_{total,\,CO_2}} - \dfrac{l_1}{P_{Pebax,\,CO_2}} \right\}} \qquad (6)$$

On the other hand, R_2 consists of two resistances which are connected in parallel. Therefore, it can be written as:

$$R_2 = \frac{l_2}{(\varepsilon P_{Pebax} + (1-\varepsilon) P_{substrate})} \qquad (7)$$

where ε is the porosity of the dense section of the substrate membrane and $P_{substrate}$ is the permeability of the substrate material that is either PES or PEI. Then, $\alpha_{2,\,CO_2/CH_4}$ can also be written as,

$$\alpha_{2,\,CO_2/CH_4} = \frac{\varepsilon P_{Pebax,\,CO_2} + (1-\varepsilon) P_{substrate,\,CO_2}}{\varepsilon P_{Pebax,\,CH_4} + (1-\varepsilon) P_{substrate,\,CH_4}} \qquad (8)$$

From (8)

$$\varepsilon = \frac{P_{substrate,\,CO_2} - \alpha_{2,\,CO_2/CH_4} P_{substrate,\,CH_4}}{\alpha_{2,\,CO_2/CH_4}(P_{Pebax,\,CH_4} - P_{substrate,\,CH_4}) - (P_{Pebax,\,CO_2} - P_{substrate,\,CO_2})} \qquad (9)$$

Using the equations derived above, ε and l_2 can be obtained for each composite membrane as follows.

1) Calculate $\alpha_{2,\,CO_2/CH_4}$ by Eq. (6) using the permeace and coated Pebax layer thickness of the composite membrane (both given in Table 1), and intrinsic permeability of Pebax and the substrate material, either PES or PEI (given in Table 2).

2) Then, calculate ε by Eq. (9) using the $\alpha_{2,\,CO_2/CH_4}$ obtained above and the intrinsic permeability data.

3) l_2 can be obtained by applying Eqs. (9) and (7) for CO_2 gas and the substrate, either PES or PEI.

MATERIALS AND METHODS

1. Materials

Pebax@ MH 1657 and PES were purchased from Arkema Inc. (France). PEI was procured from General Electric Co. (USA). Ethanol (99.5% purity), DMF (99.8% purity) and NMP (99.5% purity) as solvents were supplied by Merck Co. (Germany). The gas permeation experiments used pure CH_4 and CO_2 gases with a purity of 99.99% supplied by Mega Mount Industrial gases (Malaysia).

2. Preparation of Pebax Dense Membrane

Pebax-1657 copolymer was dried in an oven at 60 °C for 48 h to remove moisture content in the polymer. 4 wt% Pebax-1657 solution was prepared by gradually adding Pebax pellets into the solvent mixture of ethanol/water (70/30 vol/vol). To dissolve the polymer completely, the solution was vigorously stirred while solvent was refluxed at 75 °C for 4 h. Since the polymer does not dissolve in the ethanol/water mixture at low temperatures, the temperature control plays a key role in the solution preparation. After complete dissolution of polymer, the solution was gradually cooled to room temperature.

Solution casting and solvent evaporation techniques were used to prepare the dense films. Bubble-free Pebax solution was cast on the uniform and clean glass plate to a thickness of 100 μm and the solvent was evaporated to obtain a dense film. To remove the trace of solvent completely, the film was further dried at ambient temperature for 24 h and subsequently dried in an oven at 40 °C for another 24 h.

3. Preparation of Composite Membranes

Composite membranes were prepared by coating the selective thin layer of Pebax on the surface of PES and PEI substrate membranes. The substrate membranes, made of glassy polymers, play a vital role in providing the mechanical resistance to the synthesized membranes.

PES substrate membrane was fabricated by immersion-precipitation technique. PES solution (18 wt%) was prepared by dissolving the polymer in DMF under constant mechanical stirring of 200 rpm at ambient temperature. The polymer solution was sonicated for 6 h to remove air bubbles. The solution was then cast on a glass plate with an indigenously designed casting knife to a thickness of 150 μm. Then, the cast film was immersed in distilled water for precipitation, followed by immersion in fresh distilled water for 24 h to complete the solvent removal. The prepared membranes were dried for another 24 h at ambient temperature.

The procedure of the PEI support membrane preparation was the same as PES except for the polymer dope composition, which was 20 wt% PEI in DMF/ethanol (90/10 wt%) mixed solvent. Among the several methods available to prepare composite membranes such as casting, dip coating, interfacial polymerization, extrusion and press [42], the pouring on of an inclined surface method was chosen.

The substrate membrane was attached to a glass plate, which was then tilted to an angle of 45° from the horizontal surface. A small amount of dilute Pebax solution was poured onto the substrate membrane surface to flow down by gravity covering the entire substrate surface. The coated layer together with the substrate was dried at room temperature for 24 h, subsequently kept in an oven

at 40 °C for 24 h. Pebax solutions of 1, 2 and 4 wt% polymer were used to change the coated layer thickness. The composite membranes are coded as Substrate/Pebax1when 1 wt% Pebax solution is used, Substrate/Pebax 2 and 3 when 2 wt% Pebax solution is used and Substrate/Pebax 4 when 4 wt% Pebax solution is used, where the substrate is either PES or PEI.

4. Pure Gas Permeability

Gas permeation tests were performed for all the prepared membranes by using a constant pressure - variable volume system described elsewhere [43]. The membrane to be tested is placed into the membrane test cell with an effective permeation area of 13.5 cm^2. The feed gases, CO_2 and CH_4, are passed on the upstream side of the membrane and the desired pressure is maintained. The downstream side pressure is ambient pressure. By measuring the volume change with time by a bubble flow meter, the permeance of gases, P/l (GPU), is calculated from the Eq. (10).

$$\frac{P}{l} = \left(\frac{Q}{A(p_{feed} - p_{permeate})} \right) \left(\frac{273.15}{T} \right) \left(\frac{P_{permeate}}{76} \right) \times 10^6 \qquad (10)$$

where Q (cm^3/s) is the permeate flow rate, A is the effective membrane area (13.5 cm^2), p is pressure (cmHg) and T is the absolute temperature (K).

Ideal selectivity (permselectivity) of the membrane, CO_2 over CH_4, is given by the ratio of gas permeances:

$$\alpha_{2, CO_2/CH_4} = \frac{\left(\frac{P}{l} \right)_{CO_2}}{\left(\frac{P}{l} \right)_{CH_4}} \qquad (11)$$

In the case of the dense Pebax membrane, the membrane thickness is known to be 50 μm.

Therefore, the permeability, P (Barrer), can be obtained by

$$P = \left(\frac{P}{l} \right) \times 50 \qquad (12)$$

The gas permeation test was repeated four times and the average values were reported.

5. Scanning Electron Microscopy (SEM)

The morphology of the prepared membranes was investigated and also the thickness of the Pebax layer of the composite membranes was measured by scanning electron microscopy (SEM) using a SEM HITACHI, Model TM3000. Membranes were fractured in liquid nitrogen to obtain a clean cut cross-sectional view. The samples were then gold sputtered to increase electrical conductivity.

RESULTS AND DISCUSSION

1. SEM Images of the Synthesized Membranes

Fig. 3 shows the top surface images of the porous substrate membranes (Fig. 3(a) and (b)) and the PES/Pebax composite membrane (Fig. 3(c)). From Figs. 3(a) and (b), the surface of the substrate membranes looks porous with a number of dark spots.

One parameter that affects membrane morphology and its properties is polymer concentration in casting solution [44]. The pores of the PES support membrane are larger than the PEI membrane, but there are more pores at the PEI membrane surface. From Fig.
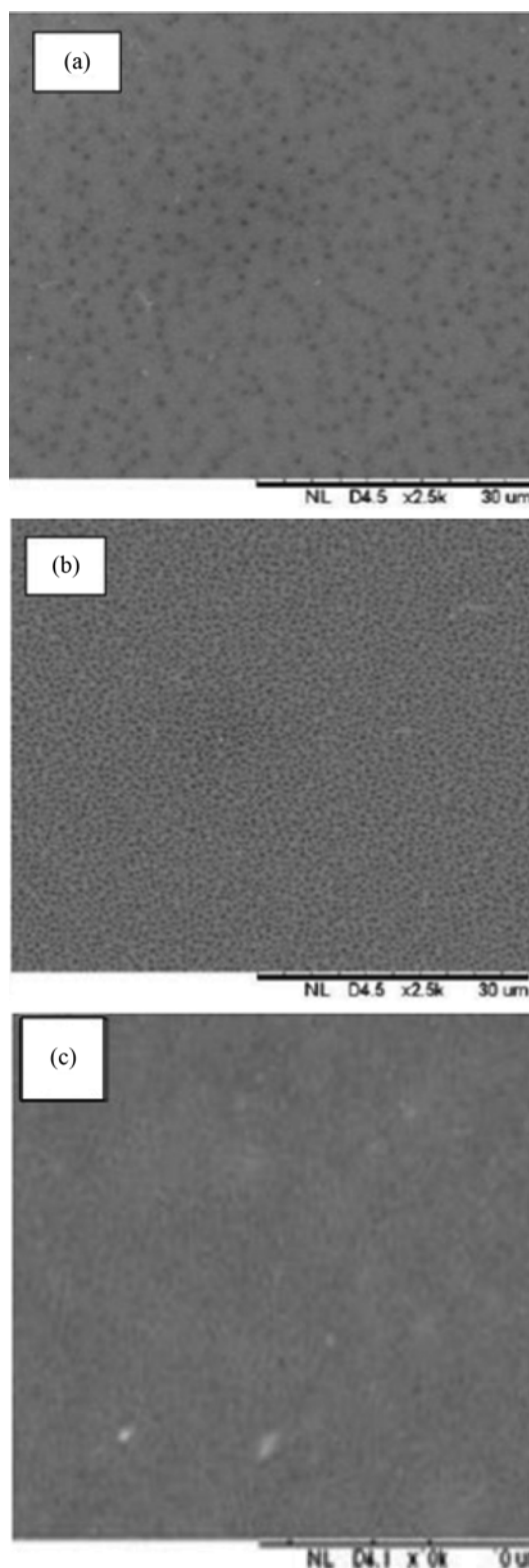

Fig. 3. SEM surface images of PES substrate membrane (a), PEI substrate membrane (b) and PES/Pebax composite membrane (c).

3(c), no pores can be observed on the smooth surface of the coated layer.

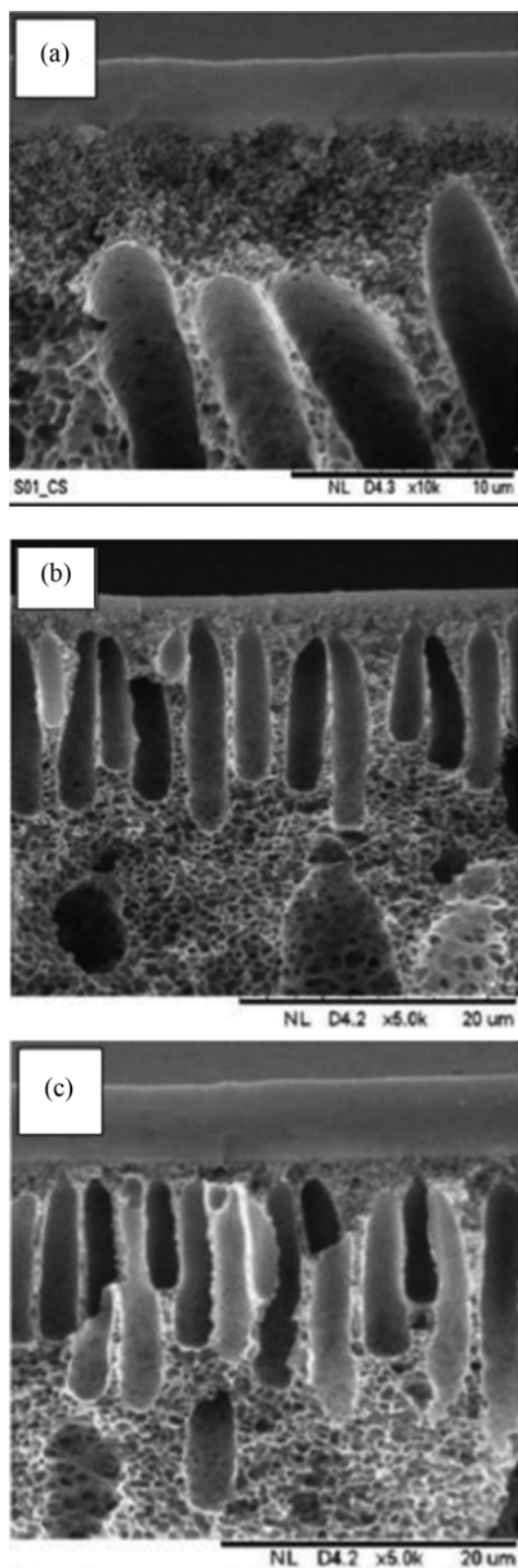The cross-sectional images of the PES/Pebax composite mem-

Fig. 4. SEM images of PES/Pebax composite membrane cross-section. (a) 1% Pebax solution coated, (b) 2% Pebax solution coated and (c) 4% Pebax solution coated.

branes, shown in Fig. 4, confirm that there are no vacant spaces at the interface between the Pebax layer and the substrate membrane.

Table 1. Summary of CO_2 permeance, CO_2/CH_4 selectivity and Pebax layer thickness

Membranes	CO_2 permeance (GPU)	CO_2/CH_4 selectivity (-)	Pebax layer thickness (μm)
PES substrate	3700±50	1.0	-
PEI substrate	4000±50	0.95	-
Pebax (dense)	1.3±0.05	26	50
PES/Pebax 1	28±1.5	24±2.3	0.5±0.05
PES/Pebax 2	17.8±1	28±2.4	1.4±0.1
PES/Pebax 3	13.5±1	27±3	1.7±0.1
PES/Pebax 4	8±0.5	31±2.1	2.6±0.2
PEI/Pebax 1	52±2	26±2.3	0.52±0.04
PEI/Pebax 2	27±1	28±2.5	1.7±0.1
PEI/Pebax 3	23±1	29±2.5	2.1±0.2
PEI/Pebax 4	15±1	30±2.5	3.5±0.2

The coated layer thickness increases progressively from Fig. 4(a) to Fig. 4(c) as the Pebax concentration in the coating dope increases. This is primarily ascribed to the viscosity effect of the Pebax solution that flows down an inclined plane, i.e., the thickness of a viscous flow is proportional to the 1/3-rd power of the kinematic viscosity.

2. Pure Gas Permeation Test

The experimental data including CO_2 permeance, CO_2/CH_4 selectivity and the top Pebax layer thickness, when available, are summarized in Table 1 for all tested membranes. Feed pressure and temperature for substrate samples were 1 barg and 25 °C and for composite membrane samples were 4 barg and 25 °C, respectively.

The table shows that the permeance of both substrate membranes is three orders of magnitude higher than the dense Pebax membrane. Since the thickness of the dense Pebax membrane was 50 μm (measured by micrometer), Pebax permeability was calculated by Eq. (12) to be 65 Barrer, which is in reasonable agreement with the literature values of 55.8 and 72 Barrer for Pebax-1657 [12,16]. As for the CO_2/CH_4 selectivity, PES substrate showed no selectivity, while the selectivity of PEI substrate was less than unity, indicating some Knudsen flow contribution. For Pebax dense membrane, the CO_2/CH_4 selectivity was as high as 26.

As for the composite membranes, the CO_2 permeance is an order of magnitude higher than the Pebax dense membrane and decreases sharply as the Pebax coating layer thickness increases for both PES/Pebax and PEI/Pebax composite membranes. The permeance of PEI/Pebax composite membrane is higher than PES/Pebax when compared at the same coated layer thickness. The CO_2/CH_4 selectivities of both composite membranes look very similar. They are less (24) or equal (26) to the Pebax selectivity of 26 when the coated layer is 0.5 μm. The selectivity tends to increase as the coated layer thickness increases, but reaches only 30-31, which is far less than the intrinsic selectivity of PES (50) and PEI (45) [45].

The experimental data were further analyzed by using the resistance model described in section 2. The objective of the analysis was to obtain ε and l_2 of the dense section of the substrate membranes to know more about their structure and its effect on the membrane performance. The permeability data required for Pebax

Table 2. Permeability of polymeric materials

Polymer		Permeability (barrer)	
		CO_2	CH_4
Pebax		65	2.50
Substrate	PES	3.4	0.068
	PEI	1.5	0.0333

Table 3. ε and l_2 obtained for each composite membrane

Composite membrane	ε (-)	l_2 (µm)
PES/Pebax 1	−0.397	-
PES/Pebax 2	0.150	0.438
PES/Pebax 3	0.283	0.864
PES/Pebax 4	0.058	0.593
Average of PES/Pebax	0.164	0.631
PEI/Pebax 1	0.780	-
PEI/Pebax 2	0.022	0.0314
PEI/Pebax 3	0.008	0.0228
PEI/Pebax 4	0.083	0.0701
Average of PEI/Pebax	0.038	0.0414

and substrate materials are listed in Table 2.

The data of ε and l_2 obtained for each composite membrane are summarized in Table 3. The data for PES/Pebax1 and PEI/Pebax1, whose coated layer thickness is 0.5 µm, are unreasonable. This is attributed to the selectivities of these membranes, which are lower than or equal to the intrinsic selectivity of Pebax. This may happen only when some pores are unfilled with Pebax and those vacant pores bring down the permeability of the intermediate layer below that of Pebax.

Therefore, only the ε and l_2 of the membranes 2, 3 and 4 were taken into consideration for both PES/Pebax and PEI/Pebax composite membranes. It was found that ε and l_2 of PES/Pebax membranes are an order of magnitude higher than those of PEI/Pebax. Thus, the porosity and the thickness of the dense section of PES substrate are much larger than those of PEI substrate. Probably, some of the pores observed at the surface of the PEI substrate (Fig. 3(b)) are not open for the gas transport. The ratios, ε/l_2, called the effective porosity, are 0.260 and 0.918 for PES/Pebax and PEI/Pebax, respectively. They are of the same order of magnitude, explaining the similarity of gas permeation properties found between the two membranes. The larger ε/l_2 value of PEI/Pebax composite membrane also explains the higher flux of PEI/Pebax than PES/Pebax.

Although the structural parameters obtained from the model calculation explains many features of gas permeation behavior, the slight increase of selectivity with an increase in the coated layer thickness cannot be explained, since the Pebax selectivity that is lower than that of the substrate material should become more dominant in governing the overall selectivity of the composite membrane as the coated Pebax layer thickness increases. One of the plausible explanations is that the Pebax layer becomes more densely packed as the Pebax concentration of the coating dope increases (to increase the Pebax layer thickness), resulting in the higher selec-

tivity of the Pebax layer.

Lastly, a simulation was made for the case when the PES or PEI substrate is coated with a silicone rubber (SR) layer. The parameters used for the simulation were as follows:

For PES substrate; l_1=2.6 µm (same as l_1 of PES/Pebax4), l_2=0.631 µm and ε=0.164 (both taken from the average value for the PES substrate)

For PEI substrate; l_1=3.6 µm (same as l_1 of PEI/Pebax 4), l_2=0.0414 µm, ε=0.038 (both taken from the average value for the PEI substrate)

For SR; P_{SR, CO_2}=3200 Barrer and $\alpha_{SR, CO_2/CH_4}$=3.4 [45]

The simulation results are;

For PES/SR composite; CO_2 permeance is 146 GPU and selectivity is 3.4.

For PEI/SR composite membrane; CO_2 permeance is 698 GPU and selectivity is 3.4.

Note that the selectivity was the same as that of SR.

It is then obvious that the strategy of composite membrane design in this work is different from that of the Henis-Tripodi membrane for gas separation. Unlike Henis-Tripodi composite membrane, in which achieving a selectivity nearly equal to that of the substrate material was aimed at, our goal was to maintain the Pebax selectivity while increasing the permeance of the composite membrane by making the coated layer as thin as possible. The porosity of the substrate membrane in this work is, therefore, made much larger than the Henis-Tripodi gas separation membrane.

CONCLUSIONS

PES/Pebax and PEI/Pebax composite membranes with different thicknesses of Pebax layer were prepared to study the effects of the thickness of the coated Pebax layer and the presence of the substitute membrane on the composite membrane performance. The following conclusions were drawn.

1) Composite membranes with selectivities almost equal to that of Pebax (26) were successfully prepared.

2) According to SEM observation, the pores of the PES substrate are larger than those of the PEI substrate.

3) According to the analysis based on the resistance model, the porosity and the thickness of the dense section of the PES substrate are an order of magnitude higher than those of the PEI substitute. However, the ratio (porosity/thickness) is greater for PEI than PES.

4) The presence of the substrate membrane lowers the gas permeance considerably when the pores are filled with Pebax, but the effect on the selectivity is not significant.

ACKNOWLEDGEMENT

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