

## PEBA/PDMS 블렌드막의 제조 및 이산화탄소 분리 특성 연구

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### Preparation of PEBA/PDMS Blend Membranes for Separation of Carbon Dioxide

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**요 약:** 본 연구는 Poly(ether block amide) (PEBA)와 poly(dimethyl-siloxane) (PDMS)를 혼합한 블렌드막(PEBA: PDMS = 5 : 2,6 : 1 wt%)을 상전이법을 이용하여 제조하여, 이산화탄소의 분리능을 향상시키고자 하였다. PDMS와 PEBA (4033)은 투과특성의 비교를 위해 각각 같은 방법의 단일막으로 제조되었고, 용매로는 *n*-butanol을 사용하였다. 제조된 막은 SEM을 이용하여 morphology를 분석하였고, 압력에 따른 CO<sub>2</sub>와 N<sub>2</sub>의 투과도를 측정하였다. 실험결과, PEBA/PDMS 블렌드막은 3기압에서 단일 PDMS막에 비해 N<sub>2</sub>에 대한 CO<sub>2</sub>의 선택도가 4~5배 높은 것으로 나타났다.

**Abstract:** Poly(ether block amide) (PEBA)/poly(dimethyl-siloxane) (PDMS) blend membranes (PEBA : PDMS = 5 : 2, 6 : 1 wt%) were prepared through the solution-casting and phase inversion process in order to demonstrate their superior performance in carbon dioxide separation. PDMS and PEBA (4033) were also prepared by the same method using *n*-butanol as a solvent. To study the gas permeation properties, the membranes were characterized with SEM and tested with carbon dioxide and nitrogen at 35°C and pressure ranging from 3 to 5 atm. In conclusion, PEBA/PDMS blend membranes were shown to have selectivity for CO<sub>2</sub>/N<sub>2</sub> separation that is 4 to 5 magnitudes greater than that of PDMS membrane at 3 atm.

**Keywords:** poly(ether block amide), poly(dimethyl siloxane), blend membrane, carbon dioxide

## 1. Introduction

Carbon dioxide, with its large emission into the atmosphere, is a major constituent of the green-house gas and separation of carbon dioxide is an important step in finding solutions to global warming. Currently, three conventional methods are used for CO<sub>2</sub> separation: absorption, adsorption, and cryogenic distillation.

However, these techniques are highly energy-consuming as well as capital-intensive methods. In an attempt to devise more energy-efficient process, recent focus has been on membrane-based gas separation which has the potential to reduce the energy consumption significantly.

Gas separation by means of polymer membranes is a pressure-driven process, where the pressure difference across the membrane needs to be maintained in order to provide the driving force necessary for the permeation. Increasing the driving force will increase the

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membrane performance, but this is at the expense of increased compression cost. Therefore, the success of this method depends on the development of new membrane with high permeation performance at a relatively low pressure that will keep the compression cost at an economic level. Many researches have been carried out in search for a suitable membrane for the separation of CO<sub>2</sub>. Thus far, PDMS has been widely used for gas separation, owing to its high gas permeation property. However, PDMS membrane is limited in that it has low selectivity for CO<sub>2</sub>.

Poly(ether block amide) (PEBA) is a family of copolymers, consisting of polyamide (PA) block as a hard segment and polyether (PE) block as a soft segment. Recently, several researchers have focused on gas permeation property of PEBA membranes [1-3]. Blume *et al.* [1] reported the permeation behavior of CO<sub>2</sub> and N<sub>2</sub> in PEBA composite membranes. The effect of PEBA's chemical composition on the permeation properties of various gases such as He, H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and SO<sub>2</sub> was investigated by Kim *et al.* [2]. Furthermore, Liu *et al.* [3] studied the permselectivity of CO<sub>2</sub>/N<sub>2</sub> through the thin-film hollow fiber PEBA/ PSf composite membrane which is composed of a thin PEBA skin layer (< 5 μm) and a porous polysulfone hollow fiber substrate to improve gas permeance. The findings from previous studies suggest that PEBA membranes are the most promising candidate to replace PDMS for its superior CO<sub>2</sub>/N<sub>2</sub> permeability ratio. This study evaluates the feasibility of PEBA membranes by investigating the relationship between the permeation behavior of CO<sub>2</sub>, N<sub>2</sub> and the chemical properties of the PEBA/PDMS blend membranes.

## 2. Experimental

### 2.1. Materials

PEBA (4033) was purchased from Atofina Canada Inc. (Oakville, Ontario) in the form of elliptic pellets. The general chemical formula of PEBA copolymers is shown in Fig. 1. PEBAX (4033) used in this study is composed of polytetramethyleneoxide (PTMO) and ny-

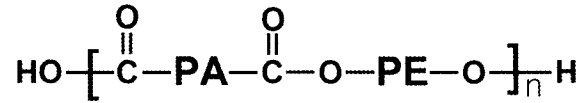


Fig. 1. The chemical structure of PEBA. PA and PE stand for an aliphatic polyamide "hard" block and a polyether "soft" block respectively.

Table 1. Physical Property of PEBAX<sup>®</sup>4033 [2]

Item	Value
PA content (wt%)	46
Density (g/cm <sup>3</sup> )	1.01
T <sub>m</sub> (PE) (°C)	21
T <sub>m</sub> (PA) (°C)	180
Crystallinity in PA block (wt%)	30
Crystalline vol% in polymer	14

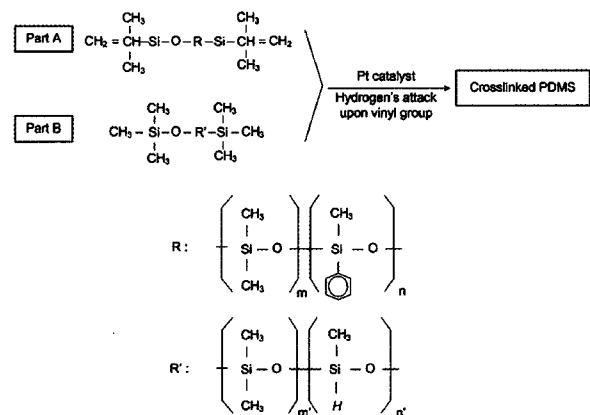


Fig. 2. The chemical structure of PDMS oligomers and a crosslinking reaction scheme of PDMS membrane.

lon 12, and its physical property is summarized in Table 1. PDMS (dimethylsiloxane, GE655) which is comprised of PDMS oligomers terminated with vinyl groups (part A) as well as a mixture of Pt catalyst and PDMS oligomer with active hydrogens (part B) was supplied by Dongyang Silicon (Seoul, Korea). The structure of PDMS (part A and part B) is represented in Fig. 2. *N*-butanol, the solvent for the preparation of PEBA and PDMS solution, was purchased from Aldrich Chemical Co. (Milwaukee, USA). All organic solvents were extra pure grade and used without any further purification.

### 2.2. Membrane Preparation

The predetermined amount of PEBA (4033) was dissolved in the solvent to prepare the casting solutions.

The polymer solution was stirred vigorously at 90°C for at least 5 hr. PDMS solution, part A and part B with a ratio of 9 : 1, were dissolved in *n*-butanol at 40°C for 3 hr. The PEBA solution and the PDMS solution were combined to prepare the mixture of PEBA/PDMS solutions with predetermined compositions (PEBA : PDMS = 5 : 2, 6 : 1 wt%). The PEBA/PDMS solutions were then stirred at 90°C for 30 min. The casting solution was poured into a Petri dish and dried in a fume hood at room temperature for 24 hr. Subsequently, the dry nascent PEBA/PDMS blend membranes were crosslinked in the oven set at 100°C for 2 hr and the membranes were peeled off from the Petri dish. Finally, the membranes were kept at 40°C for 2 days in a vacuum oven to remove any residual solvent. The thickness of the resulting dry membrane was measured to be 210  $\mu\text{m}$ .

### 2.3. Permeation Measurement

The gas permeance of the membranes was measured with carbon dioxide and nitrogen using the GPA-601 (SeptraTek Co., Incheon, Korea) [4], which is illustrated in Fig. 3. This apparatus can make the on-line measurements of both permeation transient and permeation composition during gas permeation. In addition, permeability, diffusivity and solubility coefficients from the permeation transient curves were determined simultaneously. This apparatus consists of three parts: a) feeding system, b) membrane cell, and c) measurement and data acquisition system. The permeation apparatus and the determination principle of the respective parameter from the transient are described well elsewhere [4]. For the gas permeation test in this study, the pressure difference between the feed and permeate side of the membrane ranged from 3 to 5 atm, and the cell temperature was 35°C.

## 3. Results and Discussion

Fig. 4 shows the SEM pictures of the cross-section of the PEBA/PDMS blend membranes and PEBA (4033) membrane. As seen in the figure, the number

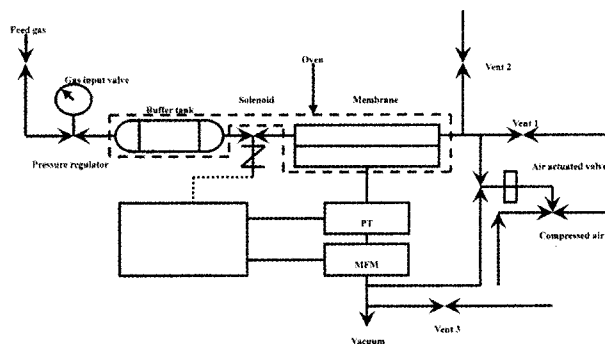


Fig. 3. A schematic representation of permeation apparatus.

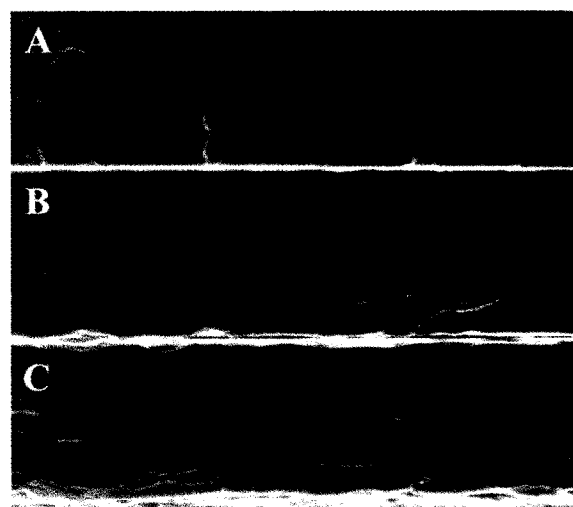


Fig. 4. SEM pictures of the cross-sections of the PEBA/PDMS blend membranes. (A) PEBA (4033), (B) PEBA : PDMS = 6 : 1 wt%, (C) PEBA : PDMS = 5 : 2 wt%.

of void in the PEBA/PDMS blend membranes increased with increasing PDMS content. This implies that the blend composition of two polymers is limited due to the difference of chemical compatibility of these. Therefore, the blend compositions of the PEBA/PDMS membranes in this study were determined 5 : 2 and 6 : 1 wt%.

The permeation behaviors of pure CO<sub>2</sub> and N<sub>2</sub> through each membrane at different operating pressure were investigated to obtain the intrinsic permselectivity of the PDMS, PEBA, and PEBA/PDMS blend membranes. Figs. 5~6 exhibit the effect of feed pressure on gas permeability at 35°C. It is well known that the gas permeabilities of the rubbery polymer membranes are higher than those of glassy polymer membranes be-

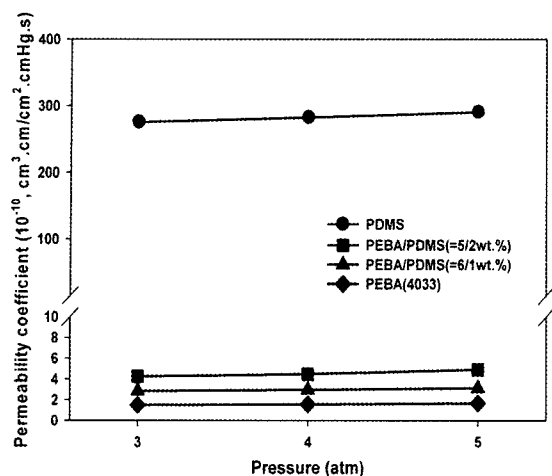


Fig. 5. Permeability coefficient of nitrogen through PDMS, PEBA : PDMS 5 : 2, 6 : 1 wt% blend and PEBA (4033) membranes at 35°C.

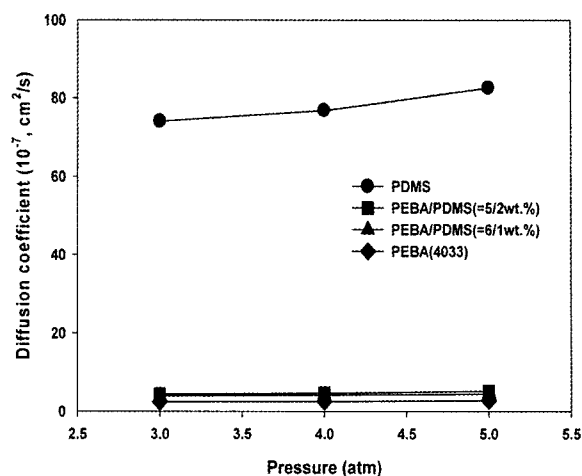


Fig. 7. Diffusion coefficient of nitrogen through PDMS, PEBA : PDMS 5 : 2, 6 : 1 wt% blend and PEBA (4033) membranes at 35°C.

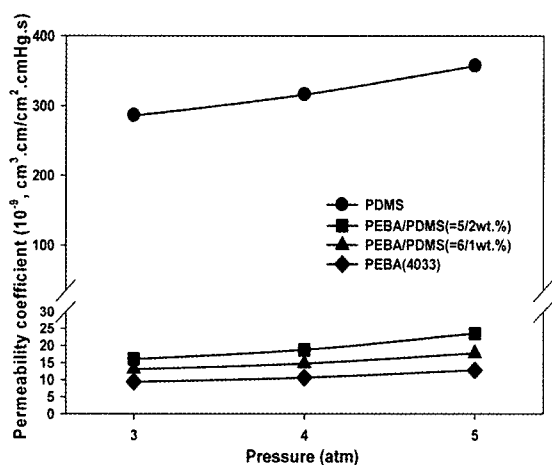


Fig. 6. Permeability coefficient of carbon dioxide through PDMS, PEBA : PDMS 5 : 2, 6 : 1 wt% blend and PEBA (4033) membranes at 35°C.

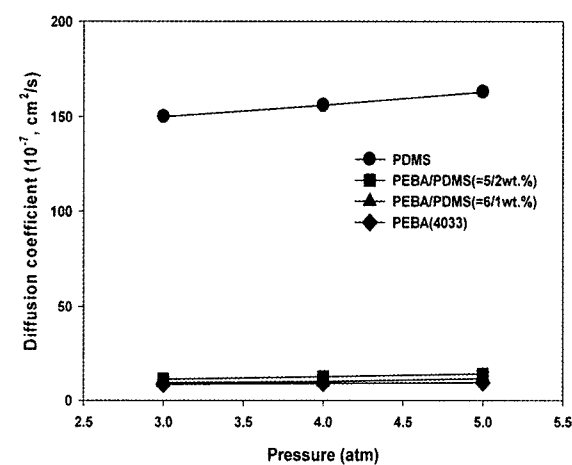


Fig. 8. Diffusion coefficient of carbon dioxide through PDMS, PEBA : PDMS 5 : 2, 6 : 1 wt% blend and PEBA (4033) membranes at 35°C.

cause of the large chain mobility of the rubbery polymer. PEBA (4033) is a copolymer comprising of 46 wt% glassy polyamide segments and 54 wt% rubbery polyether segments. Thus, the gas permeability of the blend membrane increased as the content of PDMS, a typical rubbery polymer, increased.

Additionally, the  $\text{CO}_2$  and  $\text{N}_2$  permeabilities of the PDMS membrane were much higher than those of PEBA and PEBA/PDMS blend membranes, as seen in the results. And all the  $\text{N}_2$  permeabilities through the membranes increased slightly as the feed pressure in-

creased while the  $\text{CO}_2$  permeabilities increased significantly as the feed pressure increased.

Generally, gas permeability of polymeric membrane depends mainly on both sorptional and diffusional properties. Therefore, it is of importance to investigate how the gas permeability can be affected by the two properties. Figs. 7~10 illustrate the diffusion and solubility coefficients of  $\text{N}_2$  and  $\text{CO}_2$  through membranes with feed pressure, respectively. In general, the diffusivity tends to increase with increasing operating pressure in polymeric membranes, because the driving

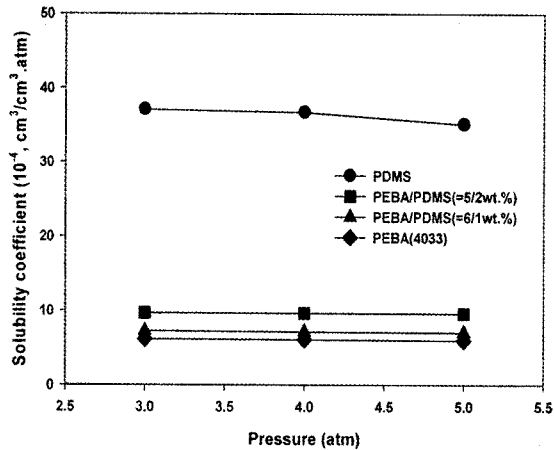


Fig. 9. Solubility coefficient of nitrogen through PDMS, PEBA : PDMS 5 : 2, 6 : 1 wt% blend and PEBA (4033) membranes at 35°C.

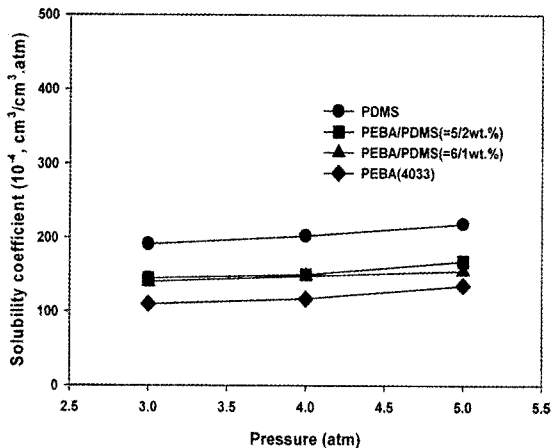


Fig. 10. Solubility coefficient of carbon dioxide through PDMS, PEBA : PDMS 5 : 2, 6 : 1 wt% blend and PEBA (4033) membranes at 35°C.

force for the permeation increases. All of the diffusivities of  $N_2$  and  $CO_2$  through the membranes increased with increasing feed pressure. Especially, the PDMS membrane showed the largest diffusivities for both  $N_2$  and  $CO_2$ , but those of the other three membranes were not so much different in magnitude. It reveals that the difference of diffusivities of the membranes containing glassy is not significant. On the other hand, it is considerable to increase the  $N_2$  diffusivity with pressure through the PDMS membrane compared to their permeability.

Fig. 9 presents the  $N_2$  solubilities of the membranes with feed pressures. With increasing feed pressure, the

$N_2$  solubility of the PDMS membrane decreased significantly while those of the other membranes decreased slightly or did not change. Also, the magnitude of the  $N_2$  solubility of each membrane was in the order of the rubbery polymer content in the membrane in the given range of feed pressure, ranked in the following order:  $S_{PDMS} > S_{PEBA/PDMS=5/2} > S_{PEBA/PDMS=6/1} > S_{PEBA}$ . In principle, it is predicted for non-condensable gases, such as  $N_2$ , having a low sorption level that the relationship between gas solubility and pressure is linear and Henry's law is applicable [4]. However, it is surprisingly noted that the  $N_2$  solubility of the PDMS membrane decreases with increasing feed pressure, implying that the sorption isotherms possess downward curvature as can be observed in the sorption behavior of glassy polymeric membranes. The reason for that is not clear but it may be related to the compactness of the rubbery membrane at high feed pressure. That is, since  $N_2$  is inert to PDMS membrane, its solubility is likely to be dependent on membrane structure rather than the interaction between  $N_2$  and membrane. Consequently, now one can see that the increasing permeabilities of  $N_2$  with increasing feed pressure must be attributed to the  $N_2$  diffusion behaviors in the membranes.

All the  $CO_2$  solubility coefficients of the membranes increased with increasing feed pressure, which was an opposite trend to the  $N_2$  solubility behaviors, as shown in Fig. 10. The sorption of the condensable gas  $CO_2$  in rubbery polymeric materials is characterized by sorption isotherms that are nearly linear, potentially with slight upward curvature with feed pressures. Thus, the increase in solubility coefficient with pressure often occurs in  $CO_2$  through the rubbery membrane [4]. Generally, when the pressure is low, the  $CO_2$  solubility of glassy polymer membrane tends to decrease with a feed pressure increase due to the competitive property of Langmuir sorption [3]. However, the  $CO_2$  solubility coefficients in the PEBA/PDMS blend membranes and PEBA membranes were dependent on the feed pressure, as shown in the result. This implies that the rubbery segment and the glassy segment in the each mem-

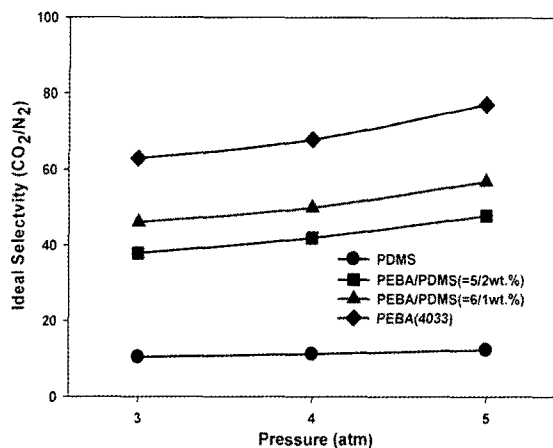


Fig. 11. Selectivity of CO<sub>2</sub>/N<sub>2</sub> through membranes.

brane may have an effect on the CO<sub>2</sub> sorption behaviors. Therefore, from the above facts, it can be inferred that the increase in CO<sub>2</sub> permeability with feed pressure might be assigned to the combined effects in the solubility coefficient and the diffusion coefficient. The selectivity of the PDMS, PEBA, and PEBA/PDMS blend membranes for CO<sub>2</sub>/N<sub>2</sub> expressed in terms of pure gas permeability ratio, ideal selectivity, is shown in Fig. 11. The selectivities to CO<sub>2</sub> over N<sub>2</sub> have a considerable incline with feed pressure in all the membranes. The PEBA membrane exhibited the highest selectivity compared to other membranes owing to PA block as glassy segment in the PEBA polymer. Also, the selectivity of PEBA/PDMS blend membranes (PEBA : PDMS = 5 : 1, 6 : 2 wt%) for CO<sub>2</sub>/N<sub>2</sub> are 4 to 5 times greater than that of PDMS membrane at 3 atm.

#### 4. Conclusions

Poly(ether block amide) (PEBA) / poly(dimethylsiloxane) (PDMS) blend membranes (PEBA: PDMS = 5 : 2, 6 : 1 wt%) can be prepared via solution casting and

phase inversion process. PDMS and PEBA (4033) were also prepared by the same method using *n*-butanol as a solvent. It is characterized by the permeation behaviors of CO<sub>2</sub> and N<sub>2</sub> through the membranes with feed pressures. Although the gas permeabilities of PEBA/ PDMS blend membranes were lower than that of the PDMS membrane, the CO<sub>2</sub>/N<sub>2</sub> selectivities were higher than that of the PDMS membrane. Therefore, this study can prove that PEBA/PDMS blend membranes have a good permselectivity for CO<sub>2</sub>/N<sub>2</sub> and they exhibit a higher permeability for CO<sub>2</sub> than that of PEBA membrane.

#### Acknowledgements

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