PBEM-POEM 공중합체와 Poly(ethylene glycol)의 폴리머 블렌드를 이용한 이산화탄소 분리막 제조

문 승 재 · 민 효 준 · 김 나 운 · 김 종 학[†]

연세대학교 화공생명공학과

Fabrication of Polymeric Blend Membranes Using PBEM-POEM Comb Copolymer and Poly(ethylene glycol) for CO2 Capture

Seung Jae Moon, Hyo Jun Min, Na Un Kim, and Jong Hak Kim[†]

Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, South Korea

요   약: 본 논문에서는 이산화탄소 친화적인 PBEM-POEM (PBE) 공중합체를 기반으로 고분자 블렌드 분리막을 제조하는 방법을 제시한다. PBE 공중합체는 자유 라디칼 중합 반응을 통해 손쉽게 합성이 가능하며, 이를 상용 고분자인 PEG와 다양한 비율로 혼합하여 이산화탄소/질소 분리막을 제조하였다. 이산화탄소/질소 분리 성능을 테스트한 결과, PEG의 함량이 높을수록 이산화탄소 투과도는 감소하는 반면 이산화탄소/질소 선택도는 크게 증가하는 상충(trade-off) 관계가 나타났다. 그러나 PBE/PEG (9 : 1)과 PBE/PEG (7 : 3)을 비교하면 이산화탄소 투과도는 단지 8.3% 감소한 반면에 질소 투과도는 69.1%나 감소하였다. 따라서 이산화탄소/질소 선택도가 33.8에서 100.3으로 크게 증가하였다. 이것은 PBE 공중합체의 80%를 차지하는 POEM 사슬이 PEG와 상호작용하여 더욱 조밀한 구조가 되었기 때문이며, 이를 FT-IR, XRD, SEM 분석으로 확인하였다. PBE/PEG (7 : 3) 블렌드 막이 가장 최적의 기체 분리 성능을 가졌고, 이산화탄소투과도는 170.5 GPU, 이산화탄소/질소 선택도는 100.3이었다.

Abstract: In this paper, we develop a polymeric blend membrane based on CO_2-philic poly(2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl] ethyl methacrylate)-poly(oxyethylene methacrylate) (PBEM-POEM) comb copolymer, which was synthesized by facile free radical polymerization. The PBEM-POEM (PBE) comb copolymer was blended with a commercial oligomer, low-molecular-weight poly(ethylene glycol) (PEG, M_w = 200 $gmol^{-1}$) with various ratios to prepare CO_2/N_2 separation membranes. From the result of CO_2/N_2 separation test of the PBE/PEG blend membranes with the various PEG contents, we could conclude that with increasing PEG content, the CO_2/N_2 selectivity significantly increased while the CO_2 permeability decreased showing trade-off relationship. However, when comparing the performance of the PBE/PEG (9 : 1) with the PBE/PEG (7 : 3) membrane, the CO_2 permeance decreased by only 8.3%, while the N2 permeance decreased by 69.1%. Therefore, the CO_2/N_2 selectivity dramatically increased from 33.8 to 100.3. This could be because the POEM chains, which account for 80% of the PBE copolymer, favorably interact with PEG and lead to a more compact chain structure, which was confirmed by FT-IR, XRD and SEM analysis. The PBE/PEG (7 : 3) blend membrane had the most optimal gas separation performance, showing a CO_2 permeance of 170.5 GPU and CO_2/N_2 selectivity of 100.3.

Keywords: blend membrane, comb copolymer, CO2, poly(ethylene glycol)

[†]Corresponding author(e-mail: jonghak@yonsei.ac.kr, http://orcid.org/0000-0002-5858-1747)

1. Introduction

Gas separation using membrane technology over the last 30 years has been commercialized for a variety of processes such as air separation, hydrogen separation and flue gas treatment[1-3]. Among these processes, CO_2 separation from gas mixtures is known as one of the most important topics because of its huge market and global warming by the greenhouse effect. Membrane technologies have attracted attention due to their low energy consumption, simple processing and environment-friendly properties[4]. Various materials have been used to fabricate gas separation membranes and polymer-based membrane was one of the most attractive membranes due to its low cost and easy processability [5-8]. However, in the case of a polymeric membrane, there is a problem due to a trade-off relationship between gas permeability and selectivity[9,10]. Therefore, various studies have been conducted to address such a problem. For example, there have been many studies on CO_2 separation polymeric membrane that were carried out to introduce polymers having functional groups with high affinity for CO_2[11-18].

Poly(ethylene glycol) (PEG) is a commercially available hydrophilic polymer, and soluble in various polar solvents such as water or alcohol. Therefore, PEG has been widely used as the hydrophilic moiety of amphiphilic block or graft copolymers. In addition, PEG has numerous ether (C-O-C) groups which can enhance the CO_2 solubility, thereby leading to an increase in CO_2 permeability when it is incorporated in the polymer membranes. This results from the strong Lewis acid-base interaction between the ether group acting as a Lewis base and the CO_2 molecule acting as a Lewis acid [18,19]. In this study, a low-molecular-weight PEG was introduced into the polymer matrix to increase the CO_2 solubility. As PEG has a high tendency to crystallize when its molecular weight is high, it becomes difficult to form a defect-free membrane. Therefore, we choose the PEG oligomer with a molecular weight of 200 $gmol^{-1}$ as an additive.

In this study, CO_2-philic and alcohol-soluble PBE comb copolymer was synthesized by free radical polymerization and blended with PEG at various weight ratios. Subsequently, the PBE/PEG blend solution was coated onto a poly(1-(trimethylsilyl-1-propyne))-coated polysulfone substrate to prepare a thin-film composite membrane. The CO_2/N_2 separation properties were measured at a constant pressure of 2 bar at room temperature (25 °C) according to the PEG loading in the blend membranes. The results were analyzed by using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental Section

2.1. Materials

2-[3-(2H-Benzotriazol-2-yl)-4-hydroxyphenyl] ethyl methacrylate (BEM, M_w = 323 $gmol^{-1}$), poly(oxyethylene methacrylate) (POEM, poly(ethylene glycol) methyl ether methacrylate, M_n = 500 $gmol^{-1}$), azobisisobutyronitrile (AIBN) and poly(ethylene glycol) (PEG, M_w = 200 $gmol^{-1}$) were purchased from Sigma-Aldrich. N,N-dimethylformamide (DMF), isopropyl alcohol (IPA) and methanol were obtained from J. T. Baker. Poly(1-(trimethylsilyl-1-propyne)) (PTMSP) was purchased from Gelest. n-Hexane was obtained from Duksan. Cyclohexane was purchased from Daejung. All solvents and chemicals were used as received without further purification.

2.2. Synthesis of PBE comb copolymer

PBE copolymer was synthesized with a weight ratio of BEM : POEM = 2 : 8. First, 2 g of BEM and 8 g of POEM were completely dissolved in 100 mL of DMF by stirring for 5 h. Then 0.002 g of AIBN was added to the solution as an initiator, followed by purging with N_2 gas. The mixed solution was placed in a 90 °C oil bath for 24 h. After reaction, the PBE solution was precipitated in IPA : n-hexane (1 : 3) mixed solvent. To purify the PBE copolymer, this precipitation process was repeated three times, and then the obtained copolymer was dried completely in a vacuum oven.

## 2.3. Preparation of PBE/PEG thin-film composite membranes

First, 30 wt% of PEG and PBE solutions were prepared respectively by using methanol as a solvent. Then these solutions were mixed together with varying the PBE : PEG ratios of 9 : 1, 8 : 2 and 7 : 3 and stirred for 5 h. Besides, 1 wt% PTMSP solution in cyclohexane was prepared, and coated onto the microporous polysulfone support (Toray Chemical Inc.) as a gutter layer using a RK Control coater (Model 101, Control RK Print-Coat Instruments Ltd., UK). After that, the PBE/PEG mixed solutions (10 : 0, 9 : 1, 8 : 2 and 7 : 3 weight ratio) were coated onto the PTMSP-coated polysulfone support. After coating, the membranes were dried in a vacuum oven overnight to remove the solvent completely. As a control group, the neat PBE membrane without a gutter layer was also prepared.

2.4. Gas permeation measurements

The gas permeance of the thin-film composite membranes was measured by using gas separation equipment provided by Airrane Co. Ltd. (Korea). Pure gas permeability (CO_2 and N_2) was measured in gas permeation units (GPU) (1 GPU = 10^{-6} cm^3 (STP) / (s cm^2 cmHg)), and the selectivity was determined by the ratio of the permeance for each component. (CO_2 permeance/N_2 permeance) Five thin-film composite membranes were tested, and the average estimated error in the gas permeation measurement was approximately.

2.5. Characterization

FT-IR spectra of the polymer blends were obtained with a Spectrum 100 spectrometer (PerkinElmer, USA) over the wavenumber range of 4,000~500 cm^{-1}. XRD patterns were measured by using a SmartLab (Rigaku, Japan). The morphologies of the polymer blends were characterized by using a JEOL-7610F-Plus field-emission scanning electron microscope (FE-SEM, JEOL Ltd., Japan).
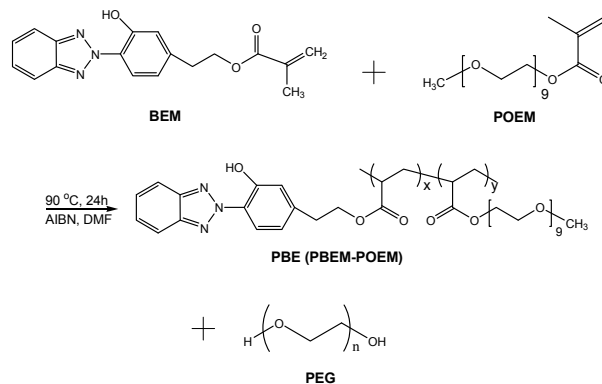
Scheme 1. Preparation of PBE/PEG blend membranes and their chemical structures.

3. Results and Discussion

3.1. Synthesis and spectroscopic characterization

The neat polymers (PBE, PEG) were mixed in three different ratios (i.e. 9 : 1, 8 : 2, 7 : 3). The PBE comb copolymer was synthesized via a one-step free radical polymerization using AIBN as the initiator, as shown in Scheme 1. This polymerization involves a relatively facile reaction. PBE chains have three tertiary amine groups in triazole which can improve the capacity for CO_2 loading through specific interactions between the basic amines and acidic CO_2. PEG has polar etheric oxygen atoms in their main chains which favorably interact with CO_2 molecules[18]. For these reasons, this polymer blends are expected to have high affinity toward CO_2, resulting in higher CO_2 solubility in the membranes.

FT-IR spectra were obtained to confirm the chemical structure and interactions of the polymer blends. The FT-IR spectra of neat PBE, PEG and PBE/PEG blends with various ratios are shown in Fig. 1. It was confirmed that the PBE comb copolymer synthesis was carried out successfully because the C=C band that appearing near 1,638 cm^{-1} was not observed in the spectrum of the PBE. The O-H stretching vibration band in the PBE (3,499 cm^{-1}) was observed at higher wavenumber than that of PEG (3,411 cm^{-1}). With increasing PEG loading, the O-H band appeared at a gradually

Table 1. Gas Permeances and CO_2/N_2 Selectivity of PBE/PEG Blend Membranes at 25 °C.

Membrane	Permeance (GPU)		CO_2/N_2 selectivity
	N_2	CO_2	
PBE (without PTMSP)	44.3	97.1	2.2 (defect)
PBE	9.9	279.4	28.1
PBE/PEG (9 : 1)	5.5	186.0	33.8
PBE/PEG (8 : 2)	2.0	98.2	50.1
PBE/PEG (7 : 3)	1.7	170.5	100.3
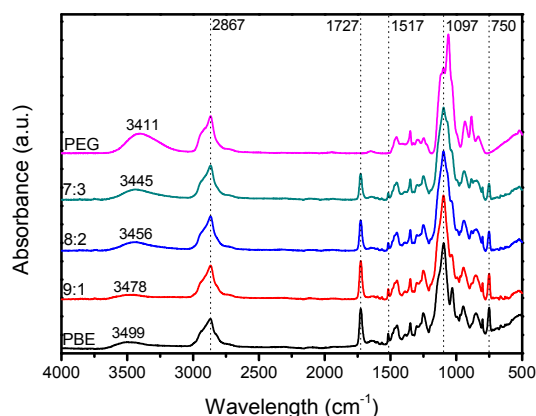
Fig. 1. FT-IR spectra of neat PBE comb copolymer, PEG oligomer, and PBE/PEG blend membranes (9 : 1, 8 : 2 and 7 : 3 weight ratios).

lower wavenumber and its intensity also increased. This is because the PBE comb copolymer and the PEG oligomer contain identical functional groups in their structures, therefore the PBE and PEG blend is expected to be a miscible and interacting system. There were no band shifts at 1,727 and 1,097 cm^{-1} corresponding to the carbonyl (C=O) groups and the ether (C-O-C) groups, respectively. It indicates that there was no hydrogen bonding between the O-H groups and the carbonyl groups nor between the O-H groups and the ether groups. The intensity of small C-C stretching vibration (in-ring) bands at 1,517 cm^{-1} and sharp C-H aromatic stretching bands at 750 cm^{-1} in PBE comb copolymer gradually decreased with increasing PEG contents, which confirms the incorporation of PEG into the PBE comb copolymer matrix.
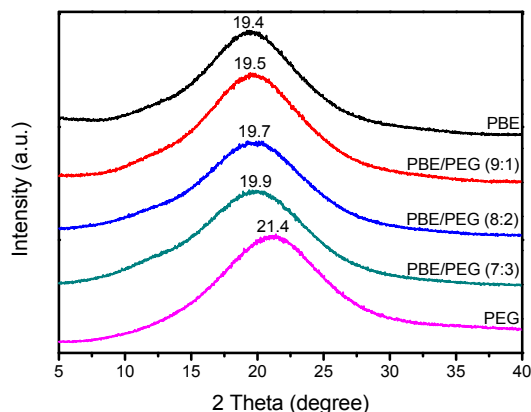
Fig. 2. XRD patterns of PBE/PEG blend membranes with various ratios.

3.2. Structural and morphological properties

The microstructures of neat PBE, PEG and their blends were characterized using XRD, as shown in Fig. 2. There was no sharp crystalline peaks, which indicates that these polymer blends have amorphous natures. The neat PBE comb copolymer exhibited one broad halo centered at $2\theta = 19.4°$, and it shifted to a higher 2θ value with increasing PEG loading. In the case of PBE/PEG (7 : 3) blend, 2θ was centered at 19.9°. According to the Bragg's law ($2\,d\sin\theta = n\lambda$), the increased 2θ causes lower d-spacing value. Therefore, the shift indicates that the d-spacing decreased with increasing PEG composition. In neat PBE, the d-spacing was determined to be 4.58 Å and that of PBE/PEG (7 : 3) blend was 4.46 Å. This phenomenon is because both POEM in PBE and PEG are hydrophilic chains, and possibly interacts with each other. These XRD results indicate that PEG oligomer interacts with the hydrophilic groups in PBE (POEM).

The morphologies of PBE/PEG blend membranes were observed using SEM, as shown in Fig. 3. According to the cross-sectional SEM images, both neat PBE and PBE/PEG (9 : 1) blend had a dense structure and there were no obvious structural defects through which gas molecules pass without selectivity. This confirms the good compatibility and miscibility between the PBE comb copolymer and PEG oligomer. The thicknesses of the selective layer were approximately 400~500 nm.
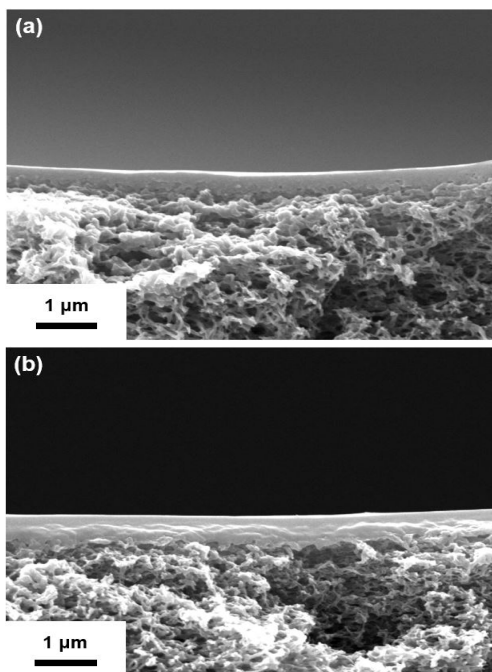
Fig. 3. Cross-sectional SEM images of (a) neat PBE and (b) PBE/PEG (9 : 1) blend membranes.
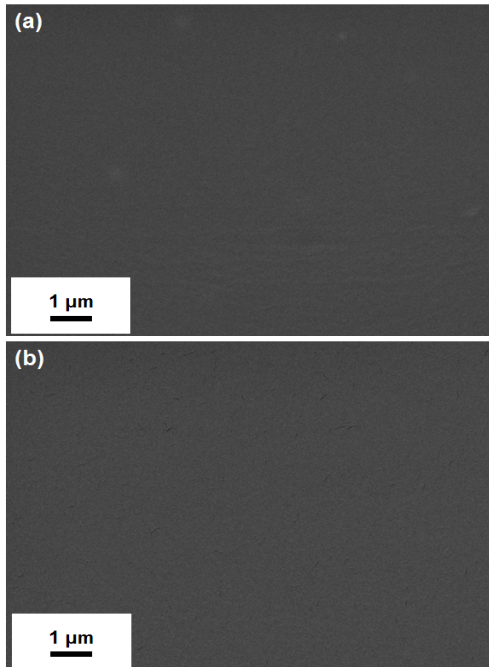

Fig. 4. Surface SEM images of (a) neat PBE and (b) PBE/PEG (9 : 1) blend membranes.

The surface SEM images are shown in Fig. 4. The membranes showed typical smooth dense polymer struc-

tures, and there was no significant difference between the neat PBE and PBE/PEG blends. It indicates that the PBE comb copolymer has high affinity for PEG oligomer.

3.3. Gas separation performances

First, the performance of neat PBE membrane without PTMSP gutter layer was measured using gas separation equipment. This membrane exhibited very low CO_2/N_2 selectivity due to the formation of structural defects. It is attributed to the penetration of PBE chains into the pores of polysulfone supports. Therefore, PTMSP with a high permeability was used as a gutter layer. When PTMSP was coated onto polysulfone support, the membranes exhibited significantly increased CO_2/N_2 selectivity. It is possible that the PTMSP gutter layer effectively prevents the PBE/PEG coating solution from penetrating through the pores of polysulfone support. It is noteworthy that PTMSP was coated with a dilute solution of 1 wt% concentration, therefore it could have little effect on the permeance of the membranes.

The pure gas permeance and CO_2/N_2 selectivity through the PBE/PEG blend membranes are shown in Table 1 and Fig. 5. The permeance of each pure gas was measured at a constant pressure of 2 bar at room temperature (25 °C). As the content of PEG increased, the CO_2 permeance decreased gradually while the CO_2/N_2 selectivity increased significantly. This might be due to the reduced distance between polymer chains, which was proved by XRD analysis. From XRD results, it was confirmed that the d-spacing decreased with increasing PEG content, which indicates that the free volume which gas molecules can pass through was reduced. Therefore, the N_2 permeance decreased at a greater rate than CO_2 permeance due to its larger kinetic diameter than CO_2[20]. The PBE/PEG (7 : 3) blend membrane showed the highest CO_2/N_2 selectivity up to 100.3 with a moderate CO_2 permeance of 170.5 GPU. This performance represents high values reported for polymer blend membranes without inorganic filler such as metal organic frameworks, zeolites, porous car-
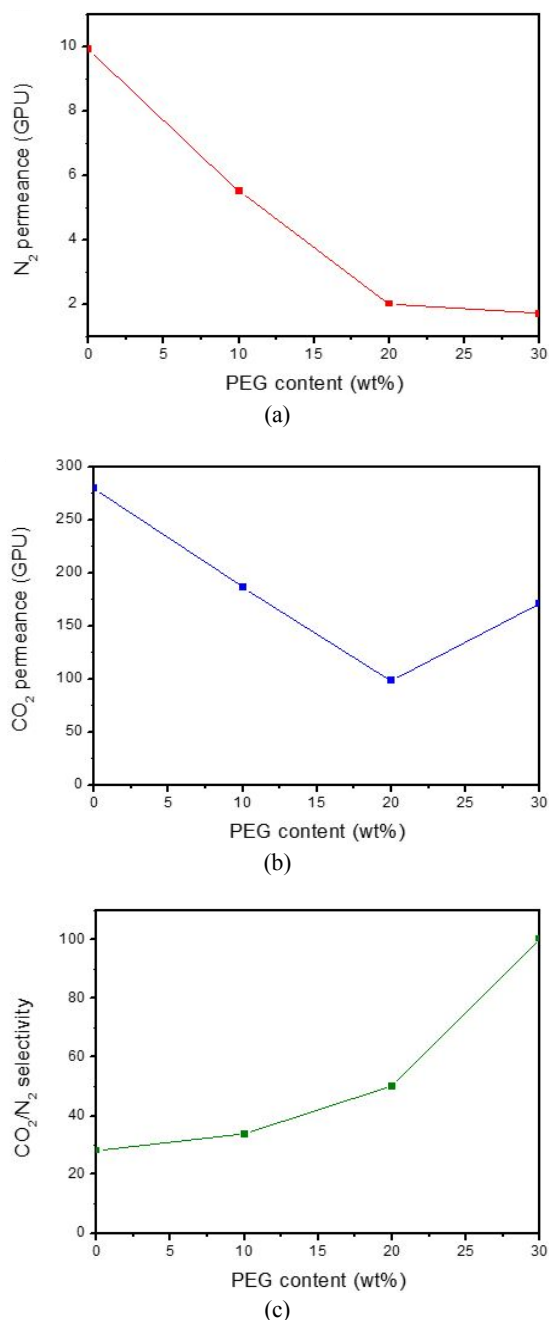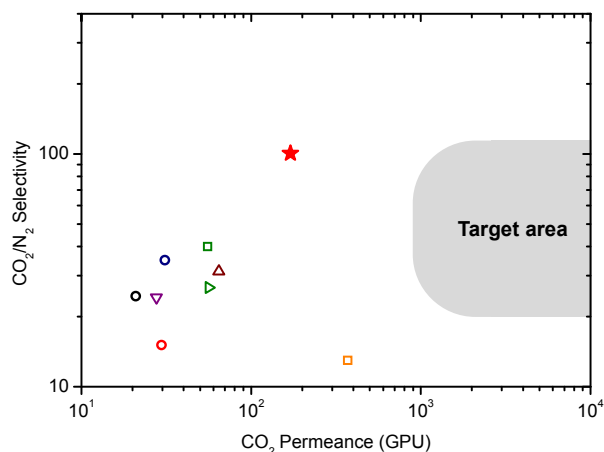
(a)

(b)

(c)

Fig. 5. Gas separation performance of PBE/PEG blend membranes according to PEG contents: (a) N_2 permeance, (b) CO_2 permeance, and (c) CO_2/N_2 selectivity.

bons or mesoporous metal oxides[21-27]. The PBE/ PEG (7 : 3) blend membrane was compared with other polymer blend membranes reported in the literatures as shown in Fig. 6.

Symbol	Membranes	Ref.
★	PBE/PEG (7 : 3)	This work
□	PDMS/PAN	[21]
○	PPE/PEG400	[22]
○	Matrimid®	[23]
□	PEO/PDMS/PVDF	[24]
○	Matrimid®/PES	[23]
▽	Pebax/PSF	[25]
△	PDMS/PSF	[26]
▷	PEG400/PTFPMS	[27]

Fig. 6. Plot of CO_2 permeance vs. CO_2/N_2 selectivity of PBE/PEG (7 : 3) membrane comparing with other polymer blend membranes reported in the literatures.

4. Conclusions

In this study, PBE/PEG blend membranes were prepared by incorporating a commercial PEG oligomer into the CO_2-philic PBE comb copolymer. The CO_2/N_2 separation properties of the membranes were analyzed according to the PEG contents. The PBE comb copolymer was synthesized via free radical polymerization, which is economical and facile reaction. Specific interactions between the PBE comb copolymer and PEG oligomer were confirmed by FT-IR analysis. Upon the incorporation of PEG into PBE comb copolymer, no significant shifts were observed in the FT-IR spectra. Furthermore, from the XRD analysis, it was confirmed that the POEM chain showed a more compact structure

as the PEG loading increased. The change in polymer structure influenced the gas permeance of the PBE/PEG blend membranes. As the PEG content increased, the gas permeability gradually decreased while the selectivity significantly increased. For the PBE/PEG (7 : 3) membrane, the CO_2 permeance decreased from 279.4 GPU to 170.5 GPU while the CO_2/N_2 selectivity increased from 28.1 to 100.3, when compared with the neat PBE.

Acknowledgements

Reference

1. R. W. Baker, "Future directions of membrane gas separation technology", *Ind. Eng. Chem. Res.*, **41**, 1393 (2002).

2. N. W. Ockwig and T. M. Nenoff, "Membranes for hydrogen separation", *Chem. Rev.*, **107**, 4078 (2007).

3. P. Bernardo, E. Drioli, and G. Golemme, "Membrane gas separation: A review/state of the art", *Ind. Eng. Chem. Res.*, **48**, 4638 (2009).

4. W. S. Chi, J. H. Lee, M. S. Park, and J. H. Kim, "Recent research trends of mixed matrix membranes for CO_2 separation Won Seok", *Membr. J.*, **25**, 373 (2015).

5. S. Kwon and J. Rhim, "Facilitated transport separation of carbon dioxide using aminated polyetherimide membranes", *Membr. J.*, **25**, 248 (2015).

6. P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, and L. Wojtas, "Porous materials with optimal adsorption thermodynamics and kinetics for CO_2 separation", *Nature*, **495**, 80 (2013).

7. D. M. D'Alessandro, B. Smit, and J. R. Long, "Carbon dioxide capture: Prospects for new materials", *Angew. Chem. Int. Ed.*, **49**, 6058 (2010).

8. C. Park, J. Lee, M. Park, and J. Kim, "Facilitated transport: Basic concepts and applications to gas separation membranes", *Membr. J.*, **27**, 205 (2017).

9. H. Lin and M. Yavari, "Upper bound of polymeric membranes for mixed-gas CO_2/CH_4 separations", *J. Membr. Sci.*, **475**, 101 (2015).

10. L. M. Robeson, "Correlation of separation factor versus permeability for polymeric membranes", *J. Membr. Sci.*, **62**, 165 (1991).

11. C. Park, J. Jung, J. Lee, and J. Kim, "Enhancement of CO_2 permeance by incorporating $CaCO_3$ in mixed matrix membranes", *Membr. J.*, **28**, 55 (2018).

12. P. Guan, J. Luo, W. Li, and Z. Si, "Enhancement of gas permeability for CH_4/N_2 separation membranes by blending SBS to Pebax polymers", *Macromol. Res.*, **25**, 1007 (2017).

13. Y. Choi and S. W. Kang, "Effect of 4-hydroxybenzoic acid on CO_2 separation performance of poly(ethylene oxide) membrane", *Macromol. Res.*, **24**, 1111 (2016).

14. W. S. Chi, S. U. Hong, B. Jung, S. W. Kang, Y. S. Kang, and J. H. Kim, "Synthesis, structure and gas permeation of polymerized ionic liquid graft copolymer membranes", *J. Membr. Sci.*, **443**, 54 (2013).

15. C. H. Park, J. H. Lee, J. P. Jung, B. Jung, and J. H. Kim, "A highly selective PEGBEM-g-POEM comb copolymer membrane for CO_2/N_2 separation", *J. Membr. Sci.*, **492**, 452 (2015).

16. S. H. Ahn, J. A. Seo, J. H. Kim, Y. Ko, and S. U. Hong, "Synthesis and gas permeation properties of amphiphilic graft copolymer membranes", *J. Membr. Sci.*, **345**, 128 (2009).

17. J. H. Lee, J. P. Jung, E. Jang, K. B. Lee, Y. S. Kang, and J. H. Kim, "CO_2-philic PBEM-g-POEM comb copolymer membranes: Synthesis, characterization and CO_2/N_2 separation", *J. Membr. Sci.*, **502**, 191 (2016).

18. A. Ghadimi, R. Gharibi, H. Yeganeh, and B. Sadatnia, "Ionic liquid tethered PEG-based polyurethane-siloxane membranes for efficient CO_2/CH_4 separation", *Materials Science and Engineering: C*,

102, 524 (2019).

19. H. Lin and B. D. Freeman, "Materials selection guidelines for membranes that remove CO_2 from gas mixtures", *J. Mol. Struct.*, **739**, 57 (2005).

20. B. D. Freeman, "Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes", *Macromolecules*, **32**, 375 (1999).

21. P. Li, H. Z. Chen, and T.-S. Chung, "The effects of substrate characteristics and pre-wetting agents on PAN-PDMS composite hollow fiber membranes for CO_2/N_2 and O_2/N_2 separation", *J. Membr. Sci.*, **434**, 18 (2013).

22. T. Hu, G. Dong, H. Li, and V. Chen, "Improved CO_2 separation performance with additives of PEG and PEG-PDMS copolymer in poly (2,6-dimethyl-1,4-phenylene oxide) membranes", *J. Membr. Sci.*, **432**, 13 (2013).

23. G. Kapantaidakis and G. Koops, "High flux polyethersulfone-polyimide blend hollow fiber membranes for gas separation", *J. Membr. Sci.*, **204**, 153 (2002).

24. Y. Wang, T. Hu, H. Li, G. Dong, W. Wong, and V. Chen, "Enhancing membrane permeability for CO_2 capture through blending commodity polymers with selected PEO and PEO-PDMS copolymers and composite hollow fibres", *Energy Procedia*, **63**, 202 (2014).

25. L. Liu, A. Chakma, and X. Feng, "Preparation of hollow fiber poly (ether block amide)/polysulfone composite membranes for separation of carbon dioxide from nitrogen", *Chem. Eng. J.*, **105**, 43 (2004).

26. A. Zulhairun, Z. Fachrurrazi, M. N. Izwanne, and A. Ismail, "Asymmetric hollow fiber membrane coated with polydimethylsiloxane-metal organic framework hybrid layer for gas separation", *Sep. Purif. Technol.*, **146**, 85 (2015).

27. F. Nie, G. He, W. Zhao, J. Ju, Y. Liu, and Y. Dai, "Improving CO_2 separation performance of the polyethylene glycol (PEG)/polytrifluoropropylsiloxane (PTFPMS) blend composite membrane", *J. Polym. Res.*, **21**, 319 (2014).