Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Polymer 47 (2006) 4501–4504

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Highly selective polymeric membranes for gas separation

Yongsok Seo [a,*], Sehyun Kim [b], Seong Uk Hong [c]

[a] Intellectual Textile System Research Center (ITRC) and School of Materials Science and Engineering, College of Engineering,
Seoul National University, Sinlimdong 56-1, Kwanakku, Seoul, South Korea
[b] Polymer Processing Technology Team, LG Chemical Ltd/Tech Center, 104-1 Moonjidong, Yousungku, Daejon, South Korea
[c] Department of Chemical Engineering, Hanbat National University, San 16-1, Deokmyeongdong, Yusungku, Daejon, South Korea

Received 12 November 2005; accepted 8 May 2006

Abstract

Polymeric membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. The goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other component. To accomplish this, we proposed a novel concept of a (universal) 'organic molecular sieve' and experimentally proved its possibility by showing that organic polymer molecules at the interface between the permeable phase and the impermeable phase play the role of molecular sieves. This resulted in a significantly improved selectivity in gas separation, in fact going over the so-called 'upper-bound' sought for the past 30 years by many researchers but without much success. Since, this is not size selective like an inorganic molecular sieve but diffusion selective (the compatibilizer works like a molecular sieve to separate one gas molecules from the other), it can be used for the preparation of polymeric membranes for separation of any gas molecules pair. Because of polymer processability, this method is quite promising for the continuous mass production of polymeric membranes for real applications, especially when the polymers are insoluble to common solvents so that solution based techniques are hard to apply. This strategy can be applicable to various separation processes of many chemicals and gases.

Keywords: Polymer composite materials; Polymeric membranes; Gas separation

1. Introduction

For a given pair of gases (e.g. O_2/N_2, CO_2/CH_4, H_2/N_2, etc.), the fundamental parameters characterizing membrane separation performance are the permeability coefficient, P_A, and the selectivity, $\alpha_{A/B}$ [1–7]. The permeability coefficient is the product of the gas flux and the membrane thickness divided by the pressure difference across the membrane. The gas selectivity is the ratio of the permeability coefficients of the two gases ($\alpha_{A/B}=P_A/P_B$). Between the selectivity and the permeability, a general trade-off relationship has been known to exist; a more permeable membrane is less selective and vice versa [3–5]. This trade-off relationship leads to an upper-bound of membrane performance. Freeman [3] theoretically verified that the polymer structure has no influence on the slope of the upper-bound or the trade-off curves because the slope parameter depends only on the penetrant (gas molecules) size ratio. He concluded that the slopes of the upper-bound are unlikely to change with further polymer development efforts. His theory coincides with the fact that not much success has been obtained in spite of a substantial effort to develop polymeric membranes overcoming the upper-bound over the past 30 years [4–7]. Some inorganic membranes, such as purely molecular sieving zeolites or carbon membranes, show superior performance, but they are quite fragile and not easily processable [8]. Hence, it is not yet clear if these materials will become economically feasible for large-scale applications [5,8]. Herein, we focus on polymer membranes that are widely used. Tested was a novel approach to prepare hybrid polymeric films including a semi-crystalline polymer as a barrier phase for gas diffusion, an amorphous polymer as a matrix, and a compatibilizer for the two. We designed and prepared polymeric composite films by using a semi-crystalline polymer (nylon 6, Ny6) as a barrier component dispersed in an amorphous matrix polymer (poly(2,6-dimethyl-1,4-phenylene oxide), PPO) and a compatibilizer (poly(styrene-*co*-maleic anhydride), PSMA).

---

[*] Corresponding author. Tel.: +82 2 880 9085; fax: +82 2 886 9671.
E-mail address: ysseo@snu.ac.kr (Y. Seo).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.05.008

2. Experimental

2.1. Materials

As a semi-crystalline polymer, a raw material, nylon 6 (Kolon 171, Korea) was used. As a matrix resin, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, a product of G.E., USA) was used. As a compatibilizer, a random copolymer between styrene and maleic anhydride, poly(styrene-*co*-maleic anhydride), containing 7 wt% of maleic anhydride was used. The compatibility checking by the movement of glass transition temperature (T_g) was not noticeable. It looks as if the compatibilizer acts more to reduce the interfacial tension as vividly shown in the morphology change.

2.2. Film preparation and characterization

After nylon 6, PPO and the compatibilizer were dried in a vacuum oven at a temperature of 100 °C for more than 24 h, they were premixed with different PSMA weight ratio while the amount of Ny6 was fixed at 20 wt%. The resulting mixture was then extruded at a process temperature of 240 °C in a Bravender twin screw extruder. A flat die was connected to an exit of the twin screw extruder and the blend was subjected to an extension with a drawing unit. The extension ratio was adjusted with the rate of the winding speed to obtain a thin film of a uniform thickness. A film with an even thickness of 100 μm having 3% error limit was used. After the film samples were installed in a testing container, and an absorption gas was discharged under a high vacuum (10^{-6} Torr) before measuring a permeation rate. In the testing apparatus, an isometric method was used in which a pressure increase in the opposite side of a side where a pressure was not applied was measured. The related process is described in detail in ASTM D1434-82. In the experiment, the upstream pressure was 1 atm and the temperature was maintained at 35 °C.

3. Results and discussion

The performance test was done for oxygen–nitrogen selectivity, which presents the greatest challenge for membrane systems because the kinetic diameters of these two gases differ only by a few tenths of an angstrom (3.46 Å for O_2 versus 3.64 Å for N_2). The permeability of CO_2 (3.3 Å)was also tested. The experiment illustrates two key features of the compatibilizer: control of morphology and molecular sieving at the interface. The transmission electron microscopy (TEM) and the scanning electron microscopy (SEM) photographs in Fig. 1 show that addition of the compatibilizer leads to improved adhesion between the dispersed semi-crystalline phase (Ny6) and the matrix (PPO), better stress transmission to the Ny6 phase and easier deformation, reduced interfacial tension, and finer dispersion of the Ny6 phase. Depending on the amount of the compatibilizer, the dispersion and the deformation of Ny6 phase vary. Addition of the compatibilizer induces finer dispersion of the semi-crystalline phase. It was found that 2 wt% of the compatibilizer brings in the optimized morphology with uniform and fine dispersion of the Ny6 phase (Fig. 1). More addition of the compatibilizer than this amount led to coalescence of the dispersed Ny6 phase and resulted in a larger and more irregularly dispersed phase size. The dispersed phase had an elongated shape due to extension during the film-forming process.

The performance of the composite films is shown in Fig. 2. The addition of the semi-crystalline Ny6 phase, which works as a barrier here, into PPO decreases the O_2 permeability compared to that of a PPO film. This is ascribed to a reduction in the cross-sectional area for the glassy matrix polymer and a decrease in the free volume of the composite film. The lower permeability suggests that there is no defect inside the membrane as well as at the interface. On the other hand, the selectivity of a binary blend film increases slightly. The selectivity of a ternary blend film containing 2 wt% PSMA is surprisingly high, exceeding the upper-bound, which has never

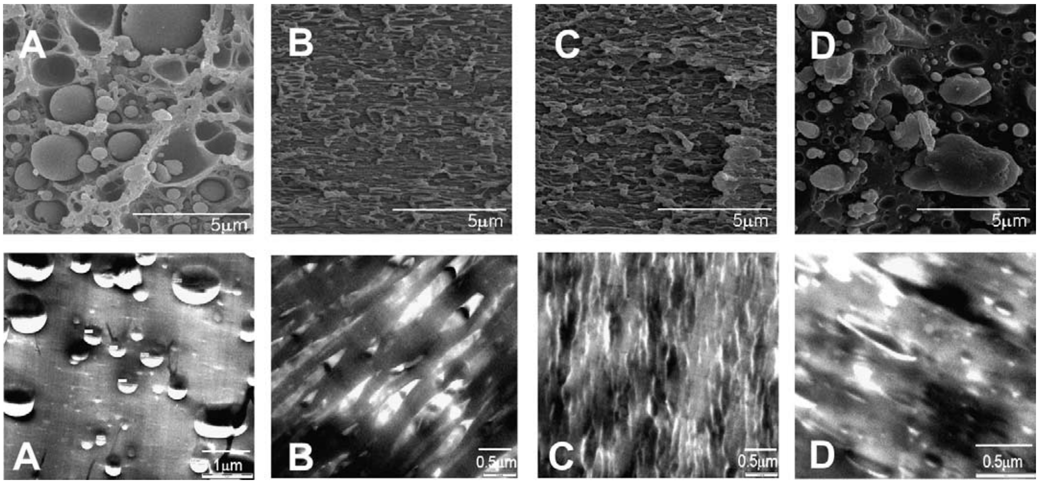

Fig. 1. Scanning electron micrographs (top row) and transmission electron micrographs of microtomed surfaces normal to flow direction (bottom row) and scanning electron micrographs (bottom row) for (A) a binary blend of Ny6 and PPO, (B) a ternary blend including 2 wt% PSMA, (C) a ternary blend including 6 wt% PSMA, and (D) a ternary blend including 10 wt% PSMA. The ternary-blend film containing an excessive amount of PSMA (more than 2 wt%) shows a coalescence of the Ny6 phase as well as PSMA own phase.

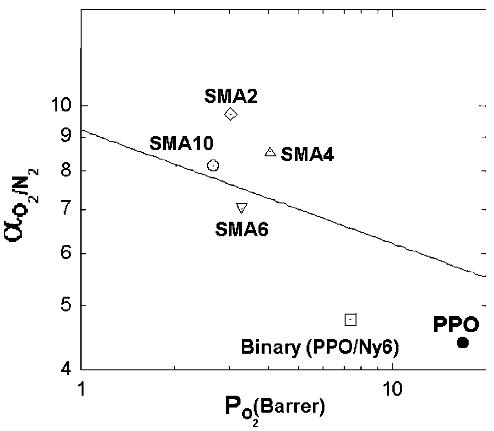

Fig. 2. The relationship between the oxygen permeability and the O_2/N_2 selectivity for PPO and Ny6 blended films. (●) PPO, (□) a binary blend, (◇) a ternary blend with 2 wt% PSMA, (△) a ternary blend with 4 wt% PSMA, (▽) a ternary blend with 6 wt% PSMA, and (○) a ternary blend with 10 wt% PSMA. The solid line is an empirical upper-bound relation. Since, the size of error bars was smaller than the size of symbols, the error bars were deleted.

happened before for this O_2 permeability range [4,5]. The permeability of this film is ca. 3 Barrer (1 Barrer $= 10^{-10}$ cm^3 (STP)cm/(cm^2 s cmHg)), which is high enough for this film to be used in an oxygen-enrichment process [8]. Addition of more compatibilizer leads to coalescence of the dispersed Ny6 phase (Fig. 1). Also the selectivity decreases with it while the permeability increases. Further addition of PSMA (more than 6 wt%) results in the formation of the PSMA own phase. Since, the selectivity of PSMA is also relatively high (P_{O_2} of PSMA = 2.4 Barrer and $\alpha_{O_2/N_2} = 7.77$), the selectivity goes up again while the permeability decreases. We emphasize here that the selectivity of 2 wt% containing PSMA film goes over the upper-bound, which is due to the action of PSMA at the interface. The maleic anhydride moiety of the PSMA is known to react with the amine end group of Ny6 forming a graft copolymer whose polystyrene part is miscible with the matrix, PPO, while the graft Ny6 part mixes with the dispersed Ny6 phase. This graft copolymer (compatibilizer) should reside at the interface surrounding the Ny6 phase as a result of the free-energy restrictions. Thus, it acts as a compatibilizer at the interface (Fig. 1). The permeants (gas molecules) should diffuse around the boundary of deformed Ny6 phase in the film since the Ny6 phase is almost a barrier, which means the permeants should pass through the channels of the compatibilizer (Here, we considered Ny6 phase as an impermeable barrier. In a strict sense, it is not perfectly impermeable since it is a semi-crystalline polymer [9]. This implicates that if there occurs some permeation of gas molecules through Ny6 phase, the selectivity after each passage through Ny6 phase would be quite high [10]. However, relatively high oxygen permeability of the present composite films excludes this possibility or it will be very little if it happens). Since, diffusion of different permeants are different in all known polymers, one that diffuses slowly because of interaction with the compatibilizer takes a longer time to diffuse through while another gas molecules diffusing faster passes through the compatibilizer phase faster. After diffusing through the compatibilizer, the permeants diffuse across the membrane until they meet the next impermeable barrier. This process results in the higher diffusive selectivity after each passage around the dispersed Ny6 phase than that of the homopolymer membrane. The same selection step occurs on and on. The thickness of the dispersed impermeable phase (Ny6) having optimized morphology is about 150 ± 50 nm (Fig. 1). Thus, the composite membrane of 100 μm can have 500–1000 layers of the dispersed phase. With increasing number of passes around Ny6 phase (hence passing through PSMA phase), the selectivity goes up and up much higher than the value previously considered to be the upper-bound. We should emphasize here that the film thickness is not the important factor but the number of dispersed phase layer across the thickness is, around which gas molecules diffuses. Though it is not size selective like an inorganic molecular sieve, the compatibilizer works like a molecular sieve to separate one gas molecules from the other; it is not selection by size exclusion [11,12]. For the composite membrane including an organic or inorganic molecular sieve compounds, the selectivity depends on the choice of a sieve having dimensions capable of discriminating gas permeants. Thus, the high selectivity for one gas pair is not necessarily guaranteed for another gas pairs [11,12]. On the other hand, present polymeric membrane is not size elective one; its high selectivity is totally based on the selectivity endowed by the compatibilizer. This is verified (vide infra) for a different gas pair of CO_2 and N_2.

The feasibility of this mechanism can be confirmed by measuring the permeability of CO_2 (P_{CO_2}) and the selectivity of α_{CO_2/N_2}. The results are shown in Table 1. The behavior of P_{CO_2} and α_{CO_2/N_2} versus P_{CO_2} follows exactly that of P_{O_2} and α_{O_2/N_2}. Addition of the semi-crystalline Ny6 phase into PPO (binary blend film) decreases P_{CO_2} compared to that of PPO film whereas it increases the selectivity α_{CO_2/N_2} a little bit. The selectivity of the ternary blend film containing 2 wt% PSMA shows a remarkable increase (α_{CO_2/N_2} slightly goes over

Table 1
Permeabilities and selectivities at 35 °C

Films	P_{O_2} (Barrer)[a]	P_{N_2} (Barrer)	P_{CO_2} (Barrer)	$\alpha(P_{O_2}/P_{N_2})$	$\alpha(P_{CO_2}/P_{N_2})$
PPO	16.8	4.1	61	4.1	14.9
PPO/Ny (20%)	7.32	1.53	24.8	4.78	16.2
PPO/NY (20%)/PSMA (2%)	3.02	0.309	12.0	9.77	38.9
PPO/NY (20%)/PSMA (4%)	4.06	0.474	17.0	8.57	35.87
PPO/NY (20%)/PSMA (6%)	3.29	0.469	12.9	7.01	27.50
PPO/NY (20%)/PSMA (10%)	2.65	0.325	11.1	8.15	34.15

[a] 1 Barrer $= 10^{-10}$ cm^3(STP)cm/(cm^2 s cmHg).

the upper-bound [13]). Though the permeability has been decreased a little bit, the selectivity increased more than twice of that of the binary blend film. Permeability of this film is high enough (12 Barrer) to be used for the removal of CO_2 [7,8,12]. Addition of more compatibilizer leads to coalescence of dispersed Ny6 phase (Fig. 1). Then, the selectivity α_{CO_2/N_2} decreased while the permeability P_{CO_2} increased. Further addition of PSMA results in the formation of PSMA own phase. High selectivity of PSMA (α_{CO_2/N_2} of PSMA is 34.64) and low permeability compared to that of PPO (P_{CO_2} of PSMA is 10.8) bring in lower P_{CO_2} and high α_{O_2/N_2}. After each passage through the compatibilizer around a dispersed phase, the selectivity of CO_2 over N_2 would go up and up and high selectivity is achieved. This result confirms the role of the compatibilizer acting like a universal organic molecular sieve for any pair of gas molecules.

4. Conclusion

The important conclusion from these experiments is that the selectivity of a morphologically optimized composite film by a compatibilizer can be much higher than the values previously considered to be the upper-bound [4,5]. It is not size selective like an inorganic molecular sieve but the high selectivity was endowed by the compatibilizer. The compatibilizer works like a molecular sieve to separate one gas molecules from the other. Hence, this strategy can be easily used to make extraordinary polymeric gas-separation membranes for all different gas pairs. Prepared and tested film can be used for oxygen gas enrichment or CO_2 gas removal as well as other gas separations. This strategy is also expected to be applicable to various separation processes of many chemicals.

Acknowledgements

We acknowledge professor Won Ho Jo at Seoul National University for helpful discussion and comments. Microscopy Center at the University of Wisconsin (Madison) is appreciated for TEM and SEM pictures. Y. Seo and S. Kim conceived the experiment, carried out the experiments and data analysis, and wrote the paper. S. Hong did the permeability measurements. This work was supported by the SRC/ERC program of MOST/KOSEF (R11-2005-065) and MOCIE(0417-20040010).

References

[1] Robeson LM. J Membr Sci 1991;62:165–85.
[2] Baker RW. Membrane technology and applications. New York: McGraw-Hill; 2000.
[3] Freeman BD. Macromolecules 1999;32:375–80.
[4] Stern SA. J Membr Sci 1994;94:1–65.
[5] Seo Y, Hong S, Lee BS. Angew Chem, Int Ed 2003;42:1145.
[6] Maier G. Angew Chem, Int Ed 1998;37:2960–74.
[7] Zimmerman CM, Singh A, Koros WJ. J Membr Sci 1991;252:1412–5.
[8] Koros WJ, Mahajan R. J Membr Sci 2000;175:181–96.
[9] Freeman BD. Polym Prepr 1999;40:478–9.
[10] Kajiyama T, Kikuchi H. J Membr Sci 1988;36:243–55.
[11] (a) Won J, et al. Adv Mater 2005;17:80.
(b) Won J, Yoon Y, Kang YS. Macromol Res 2002;10:80.
[12] (a) Singh A, Koros WJ. Ind Eng Chem Res 1996;35:1231.
(b) Vu DQ, Koros WJ, Miller SJ. Ind Eng Chem Res 2002;41:367.
[13] Yang L, et al. Polymer 2001;42:2021–9.