Angewandte
Chemie

Gas Separation

Overcoming the "Upper Bound" in Polymeric Gas-Separation Membranes**

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Polymer membranes are used commercially to separate air, to remove carbon dioxide from natural gas, and to remove hydrogen from mixtures with nitrogen or hydrocarbons in petrochemical processing applications.[1–8] For a given pair of gases (e.g., O_2/N_2, CO_2/CH_4, H_2/N_2), the fundamental parameters characterizing membrane separation performance are the permeability coefficient, P_A, and the selectivity, $\alpha_{A/B}$. 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 ($\alpha_{A/B} = P_A/P_B$), where P_A is the permeability of the more permeable gas and P_B is the permeability of the less permeable gas. For high-performance polymer membranes, both high permeability and selectivity are desirable because higher permeability decreases the size of the membrane area required to treat a given amount of gas, thereby decreasing the capital cost of membrane units, and because higher selectivity results in a higher purity product gas. However, it is well known that polymers which are more permeable are generally less selective and vice versa. A rather general trade-off has always existed between permeability and selectivity. Robeson[1] has quantified this notion on the basis of an exhaustive literature survey by plotting the available data. According to Robeson,[1,2] the upper bound performance characteristics can be described by an empirical equation; $\alpha_{A/B} = \beta_{A/B} P_A^{\lambda A/B}$, where $\lambda_{A/B} < 0$ which indicates that, as the permeability of an upper bound polymer to gas A, P_A, increases, the selectivity of the polymer for gas A over gas B, $\alpha_{A/B}$, decreases. This is the so-called trade-off. In a recent work, Freeman[3] theoretically justified the reason for this trade-off. His model suggests that

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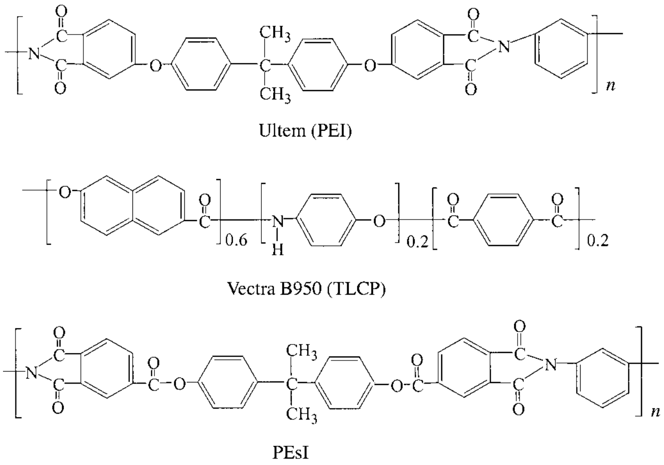
[**] We thank Drs. G. Maier (Technischen Universität München), W. J. Koros (Georgia Institute of Technology), I. Lee, S. M. Lee, J. M. Hong, and Y. S.Kang (KIST) for discussion and experimental help. This work was supported by KIST and BIONAST (Y.S.), KOSEF through AMAREN (S.U.H.).

the slope of the upper bound is a natural consequence of the strong size-sieving nature of stiff-chain glassy polymeric materials. Interestingly, the polymers that define the "upper bound" relation are stiff-chain amorphous glassy polymers. The Freeman model implies that polymer structure has no influence on the slope of the upper-bound or trade-off curves since the parameter $\lambda_{A/B}$ depends only on penetrant size ratio.[3] He concludes that the slopes of the upper-bound lines are unlikely to change with further polymer development efforts. Over the past 30 years, a substantial research effort has been directed to overcoming the limit imposed by the upper bound; chemically different polymers and various techniques, such as surface modification[1,2] have been used, but without much success.[5,6] Though some inorganic membranes, such as purely molecular sieving zeolites or carbon membranes show superior performance, it is not yet clear if these materials will become economically viable for large-scale applications.[4] Besides they are quite fragile and not easily processable. Herein, we focus on polymer membranes that are widely used; we present a novel approach based on preparing hybrid polymeric films that included a thermotropic liquid-crystalline polymer(TLCP) and a compatibilizer in the polymer matrix. Although some studies have been carried out on TLCP membranes,[7–11] to date TLCP composite membranes have not received much attention.



Scheme 1. Chemical structures of the polymers Ultem (matrix), Vectra B950 (TLCP, barrier), PEsI (compatibilizer)).

We designed and prepared composite films by using a TLCP (poly(ester amide)), a thermoplastic matrix (poly(ether imide), PEI), and an amorphous compatibilizer (a poly(ester imide), PEsI). Chemical structures of these polymers are shown in Scheme 1. The TLCP content was kept at 10 wt% while the amount of PEsI was varied. TEM photographs in Figure 1 show that addition of the compatibilizer leads to improved adhesion, better stress transmission, reduced interfacial tension, hence, finer dispersion of the TLCP phase as well as easier deformation.[12,13] It is also evident that the amount of compatibilizer plays an important role in the dispersion and the deformation of the TLCP phase. Adding a certain amount of compatibilizer induces a finer dispersion of the TLCP phase. It was found that 0.6 wt% of the compatibilizer was the optimum amount when 10 wt% TLCP was included.[12,13] Coalescence of the TLCP phase was observed when excessive amount of the compatibilizer was used (Figure 1 A c and B c), which results in a larger dispersed-phase size. The SEM images show films containing stripes resulting from the biaxial orientations.

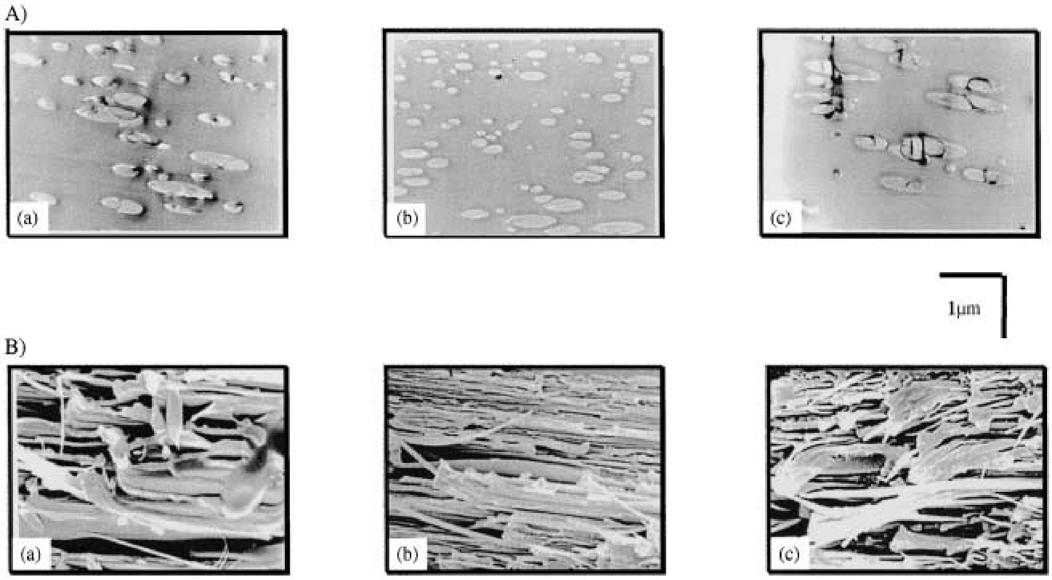


Figure 1. Transmission electron micrographs of microtomed surfaces normal to flow direction (A) and scanning electron micrographs of fractured surface parallel to flow direction (B) in each case: a) a binary blend of TLCP and PEI, b) a ternary blend including 0.6 wt% PEsI, and c) a ternary blend including 1.3 wt% PEsI, this film which contains an excessive amount of PEsI shows a coalescence of the TLCP phase.

The performance test was done for oxygen–nitrogen separation, 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).[7] The pure gas permeabilities of O_2 and N_2 were measured for all of the films at 1 atm (upstream

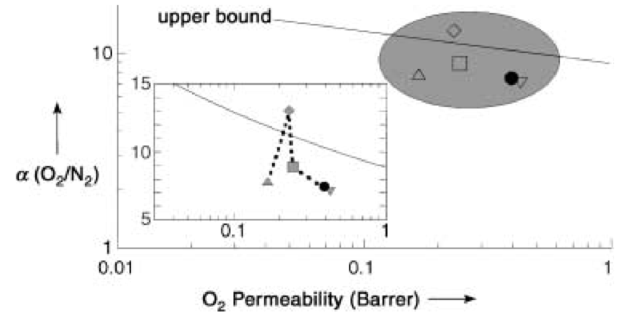


Figure 2. The relationship between the oxygen permeability and the O_2/N_2 selectivity for PEI and TLCP blended films. (▽) PEI, (●) PEI literature value,[14] (□) a binary blend, (◇) a ternary blend with 0.6 wt% PEsI, and (△) a ternary blend with 1.3 wt% PEsI. The solid line is an empirical upper bound.[1–3] Numerical values are provided in the Table 1. The inset shows the shaded region with a linear y-axis scale. The dashed line is a guide for the eyes.

pressure) and 35 °C, and Figure 2 shows the performance of the composite films. The O_2 permeability and selectivity for PEI, which were measured in this study, are in good agreement with the values reported in the literature.[14] The addition of the almost impermeable TLCP phase to PEI slightly, but not greatly, decreases the O_2 permeability compared to that of PEI film. This is ascribed to a reduction in the surface area for the glassy polymer (PEI) caused by migration of the TLCP phase to the surface[12] and thus to a slight decrease in the free volume of the composite film. On the other hand, the selectivity of the binary film increases significantly. The selectivity of the ternary blend film containing 0.6 wt% PEsI exceeds the upper bound, which has never happened before for this O_2 permeability range. In addition, the permeability of this film was not noticeably different from that of the binary-blend film. This is the first time that a dramatic increase has been observed in the selectivity of the O_2/N_2 pair without the permeability being significantly sacrificed (Table 1). Because the compatibilizer acts at the interface to reduce the interfacial tension between the TLCP phase and the matrix, it induces a fine dispersion of the TLCP phase (see Figure 1) and the number of the dispersed phase in the matrix for the compatibilized ternary system is much more than that for the binary (uncompatibilized) blend system.[12,13]

We consider two roles of the TLCP phase dispersed in the matrix polymer; an almost impermeable barrier and a very low-permeable, but highly selective, layer. Both of which are possible.[7] First, we consider the TLCP phase as an impermeable barrier. In both actual and idealized membranes which contain impermeable flakes, diffusion is retarded because diffusing gases must take tortuous paths around the impermeable flakes.[15,16] Most diffusion occurs around the nearest boundary. The solute diffuses around this boundary and across the membrane until it meets the next random flake. In our work, we used a compatibilizer for the uniform dispersion of the TLCP phase. The boundaries of the impermeable flakes are surrounded by a compatibilizer, which should exist there as a result of free-energy restrictions.[12] If the compatibilizer is amorphous, the diffusing gas molecules will pass through it, thus making it a channel that the diffusing gas must use.[13] Since diffusion of different permeants are different in all known polymers, one that diffuses slowly takes a longer time to pass through while another passes through faster (Figure 3). The concentration of the fast-diffusing molecules through the compatibilizer goes up after each passage around a dispersed TLCP phase. It is like a chromatography having many separation steps. As shown in Figure 1, a ternary-blend film containing 0.6 wt% PEsI has a small and uniformly distributed TLCP phase because of the compatibilizer, which is located at the boundary of the TLCP phase. Since almost none of the gas molecules diffuse through TLCP phase, most diffusion occurs around the nearest boundary, where the amorphous compa-

Table 1: O_2 permeability, N_2 permeability, and selectivity of PEI and blended films.

Film	$P(O_2)$ [Barrer]	$P(N_2)$ [Barrer]	$\alpha(O_2/N_2)$
PEI (ultem)[a]	0.400	0.053	7.6
PEI (ultem)[b]	0.432	0.060	7.2
binary	0.246	0.027	9.2
ternary (0.6% PEsI)	0.234	0.018	13.0
ternary (1.3% PEsI)	0.170	0.021	8.0

[a] The values reported in the literature.[14] [b] Values obtained in this work.

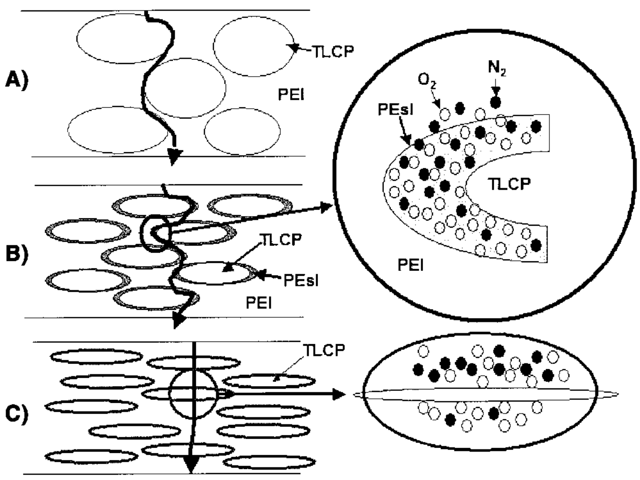


Figure 3. Solute-molecule diffusion through the composite films. The total volume of the TLCP phase is the same in all cases. A) The binary-blend film has a large TLCP phase because TLCP is immiscible with the matrix. Permeant molecules pass around the impermeable TLCP phase. B) A ternary-blend film has a small and uniformly distributed impermeable TLCP phase because of the compatibilizer. In the ternary composite films, the gas molecules must pass around the dispersed TLCP phase and pass through the PEsI phase which lies at the interface between the matrix and the dispersed phase. The inset shows a representation of gas molecules diffusing in the PEsI phase which is exaggerated for clarity. The gas molecules of larger size diffuse more slowly while those of smaller size diffuse more rapidly.[2,3]. Thus, the selectivity becomes larger than the value for the corresponding binary blend film. C) The thin TLCP phase acts as a very low-permeable highly selective phase. The inset shows a representation of gas molecules diffusing through very thin TLCP phase.

tibilizer, PEsI, is mostly located.[13] Based on the free-volume calculation, PEsI is expected to have a higher selectivity than PEI.[17] With increasing number of passes around TLCP flakes, the difference between the diffused amounts of the different gas molecules becomes larger and larger (Figure 3); hence, the selectivity is increased. When 1.3 wt% PEsI was added, both the selectivity and the permeability dropped because the dispersed TLCP phase has poor morphology as a result of coalescence or coagulation (Figure 1). The selectivity of morphologically optimized composite films having a compatibilizer, in which different gas molecules diffuse with different rate, can be theoretically much higher than the value previously considered to be the upper bound.

Second, we consider the thin TLCP phase to be very low-permeable phase but highly selective one. The concentration of more permeable gas molecules increases while it is passing through each TLCP phase. Even though the amount of the permeant going through each TLCP phase is small, the total amount will increase; thus, the selectivity will also increase. Paul and co-workers reported that a Vectra-type membrane shows a high O_2/N_2 selectivity with very low O_2 permeability (16 at 4.7×10^{-4} Barrer; 1 Barrer $=10^{-10}$ cm(STP)cm/(cm^2 sec cmHg)).[7] After each passage the relative concentration of O_2 increases (Figure 3). The amount of diffused gas molecules is very small but the diffused gas contains more O_2 than N_2 because of the high selectivity of TLCP. The selectivity increase in the binary film can be also ascribable to this mechanism. Thus, the resulting composite films containing 0.6 wt% PEsI, which has a lot of small and uniformly distributed TLCP phase because of the compatibilizer, exhibited unusually high selectivity, overcoming the upper-bound limit without any significant sacrificing of the permeability. When excessive PEsI (1.3 wt%) was added, both the selectivity and the permeability dropped because of the poor morphology. We emphasize that the important factor is not the film thickness but the number of dispersed TLCP phases. A similar idea was suggested by Robeson and co-workers a few years ago.[2] They suggested that the upper bound could be overcome if a highly permeable polymer were to be surface modified such that the surface modification created a highly selective layer. Similar in construction, a mixed-material composite (MMC) membrane with tightly packed submicron molecular sieve was reported to improve the selectivity for the oxygen/nitrogen separation,[4] but there are problems with MMC membranes such as, poor adhesion between the polymeric phase and the molecular-sieve phase.

Currently we are not sure which mechanism is more feasible, both are possible. To clarify this issue, the performance of PEsI and VB membranes should be investigated. Though difficult because both membranes are hard to make (PEsI is easily broken and VB is hard to process), we are currently investigating this. The results will be reported in the future.

The combination of the compatibilizer's role of controlling the morphology and selecting different gas molecules and the TLCP's role as a barrier and/or in allowing the diffusion of various gas molecules at different rates allowed us to experimentally show that the limit imposed by what was considered to be an upper bound could be overcome. This strategy can be easily used to make extraordinary polymeric membranes. The result should stimulate researchers to use this method for practical applications in gas-separation processes.

Experimental Section

The TLCP used in our experiments was a copolyester amide of 6-hydroxy-2-naphthoic acid (60%), terephthalic acid (20%), and 4-amino phenol (20%), commercially known as Vectra B950 (VB), manufactured by Celanese Hoechst. Poly(ether imide) (PEI), commercially known as Ultem 1000, an amorphous polymer having a high glass-transition temperature and made by General Electric, was used as the matrix. A poly(ester imide) (PEsI) synthesized in our laboratory was used as a compatibilizer. Details of its synthesis and miscibility with VB and PEI, as well as its activity as a compatibilizer were fully described elsewhere.[12,13] The TLCP content was kept at 10 wt% while the amount of PEsI was varied. After the polymers were blended in a twin-screw extruder, the blended melt was blown into a parison. Films having thicknesses of 0.04 mm were taken for the gas-permeability test. The film samples were mounted in the test cell and thoroughly degassed under very high vacuum before they were used in the permeability tests. An established constant-volume method[4,6,7] was used in the test system to measure the gas flux on the low-pressure side of the membrane.

Received: August 19, 2002
Revised: January 3, 2003 [Z19995]

Keywords: gas separation · liquid crystals · membranes · polymers · thin films

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