CO_2 Plasticization of Polyethersulfone/ Polyimide Gas-Separation Membranes

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This work reports the CO_2 plasticization of gas-separation hollow-fiber membranes based on polyimide and polyethersulfone blends. The feed pressure effect on the permeance of pure gases (CO_2, N_2) and the separation performance of a gaseous mixture (CO_2/N_2, 55/45%) is examined. Contrary to dense membranes, the permeance of CO_2 through ultrathin asymmetric fibers increases immediately with pressure resulting in pronounced apparent plasticization and reduction of the ideal CO_2/N_2 selectivity. However, no evidence of plasticization was observed when a CO_2/N_2, 55/45% mixture was fed to the hollow-fiber membranes. In all cases, CO_2 permeance decreased with pressure, while that of N_2 remained constant. Experimental results were validated by means of mathematical modeling. Membrane-separation performance was overestimated when pressure-independent permeabilities were used in the model, while pressure-dependent permeabilities, due to the overall effect of plasticization and competition phenomena, explained excellently, the obtained stage-cut and permeate purity.

Introduction

Currently, the vast majority of commercial gas-separation membranes are prepared from specific glassy polymers such as polysulfones, polycarbonates, and polyimides. These materials exhibit high selectivity coefficients, H_2/CH_4: 100–150, O_2/N_2: 5–8, CO_2/N_2: 25–45, and acceptable permeability values, H_2: 10–50 Barrer, O_2: 1–0 Barrer (Koros and Chern, 1984; Porter, 1990; Robeson, 1991; Ho and Sirkar, 1992; Baker, 2002). Despite their relatively high glass transition temperatures, 150–400°C (Stern, 1994), the maximum operating temperature of the respective membrane modules is about 100°C, due to thermal limitations imposed by module sealing/potting and membrane coating materials. Moreover, glassy polymers are seriously affected by highly sorbing gases, such as CO_2, which above a given partial pressure can plasticize the polymer matrix (Chiou et al., 1985; Wessling et al., 1991; Houde et al., 1992; Sanders et al., 1992; Bos et al., 1999). Evidences of membrane plasticization are (1) the increase of gas permeability with feed pressure, (2) the reduction of permselectivity coefficients, and (3) the suppression of glass transition temperature. While many condensable gases can cause plasticization (H_2S, C_xH_y) special attention has been given to CO_2, mainly due to the fact that this gas is encountered in many industrial gas-separation processes such as natural-gas sweetening, enhanced oil recovery, and landfill gas upgrading. Plasticization of glassy polymers can be suppressed by three alternative methods: (1) blending with a less plasticizable polymer, (2) chemical cross-linking, and (3) thermal treatment. In the first method, the polymers of polysulfone and copolyimide P84 have been proposed as strong antiplasticizing agents (Kapantaidakis et al., 1996, 1999; Bos et al., 1998a, 2001). These two glassy materials were examined in the form of dense flat-sheet membranes and proved to be completely insensitive to CO_2 sorption, even at very high feed pressures (30–50 bar). Polymer blending can be effective only when the selected polymers are miscible due to specific interactions and the resulting membranes have adequate mechanical strength. For thermodynamic reasons, most of the binary or multicomponent polymeric systems are immiscible and, therefore, tend to phase separate.

Chemical cross-linking modifications can be performed either at a high (150–300°C) or at relatively low temperatures

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(~ 80°C). In the first case, Bos et al. (1998b) suppressed the plasticization behavior of pure polyimide (Matrimid 5218) membranes by forming a so-called semi-interpenetrating network with oligopolyimide containing acetylene groups. The cross-linking was integrated by a heat-treatment step at 265°C. In another research work, Staudt-Bickel and Koros (1999) proposed that copolyimides with strong polar groups, such as carboxylic acids, can be cross-linked by reactions between ethylene glycol and the diamino benzoic acid (DABA) at 150°C. The resulting hydrogen bonding suppressed considerably the swelling effect of CO_2 in the examined polyimides. In both cases, the suppression of CO_2 plasticization after the heat-treatment step was combined with a reduction in gas permeability mainly due to the compaction and densification of the membrane structure. This problem was dealt with in a patent from DuPont, where the chemical cross-linking of polyimides is achieved by immersion of the membranes in an amino compound solution, followed by a thermal treatment at only 80°C (Hayes, 1991).

Finally, a simple thermal curing (annealing) step at 200–300°C was proposed by Krol et al. (2001) as being sufficient enough to suppress propylene plasticization in asymmetric polyimide (Matrimid 5218) hollow fibers.

Most of the research on plasticization of gas-separation membranes has been performed in flat-sheet dense membranes. There are remarkably few scientific articles dealing with the permeation of pure gases, and especially gaseous mixtures through ultrathin asymmetric hollow-fiber membranes at high feed pressures. It should be mentioned, however, that polymer membranes with very thin-skin layers (~0.1 μm) may show different physicochemical properties and permeation characteristics when compared with the respective thick (~100 μm) films. For example, Keddie et al. (1994) showed that the glass transition temperature of supported polystyrene films decreases considerably with film thickness, especially in the region between 0.01 and 0.1 μm. Pfromm and Koros (1995) also found that thin (0.5 μm) polysulfone and polyimide films exhibit significant evidence of accelerated physical ageing. To the contrary, substantially thicker films (2.5 and 28.5 μm) from the same material and with an identical history did not show such effects, at least for the observed time scales. In another work, dense films of poly(vinyltrimethylsilane) (PVTMS) and poly(trimethylsilylnorbornene)(PTMSNB) having thickness in the range of 5 to 150 μm were studied for their permeation properties and physicochemical characteristics. Membranes with lower thickness resulted in higher film densities, lower gas diffusion coefficients, and in general higher solubility coefficients (Shishatskii, 1996). In a more recent work by Wessling et al. (2001), it was also shown that the plasticization behavior of polyimide/polydimethylsiloxane composite membranes is also thickness dependent. The same material (Matrimid 5218) in the form of flat-sheet dense (50 μm) membranes was plasticized at a partial feed pressure of 12 bar, while in the form of thin (polyimide ~1 μm)/PDMS composite membrane the CO_2 plasticization was accelerated. Slightly thicker membranes (~3 μm) showed a higher resistance to CO_2 swelling.

The scope of this work is to investigate the plasticization phenomena of ultrathin (0.1–0.2 μm) hollow-fiber membranes prepared from polyethersulfone (PES) and polyimide (PI) blends. These two polymers are completely miscible (Liang et al., 1992), exhibit complementary permeation properties, plasticization behavior, and cost. In the form of dense membranes, PES is less permeable than PI, but it is plasticized at 25-bar feed pressure of pure CO_2 while the respective value for PI is 12 bar. The commercial price of polyimide (Matrimid 5218) is about 360 €/kg, while that of PES (Sumikaexcel) is 12 €/kg (prices 10/2001). Both pure gases (CO_2, N_2) and a gaseous mixture of CO_2 and N_2, 55/45%, are examined at feed pressures ranging from 4 bar to 26 bar, and at stage-cut values from 0.01 to 0.1. The performance of the blended hollow-fiber membranes in the separation of the binary mixture is compared with the predictions of mathematical modeling.

Experimental Studies

Hollow-fiber preparation

PES/PI 80/20 and 20/80 wt. % hollow fibers were spun by using only one common solvent and the dry/wet phase inversion process as described in detail by Kapantaidakis and Koops (2002). In the past, Chung et al. (1997) prepared pure polyethersulfone hollow-fiber membranes with a skin layer of about 500 Å. They showed that the addition of a nonsolvent in the spinning dope is not the precondition to form asymmetric hollow fibers with ultrathin skin layers. It was proposed that a polymer dope starts to exhibit significant chain entanglement at a critical polymer concentration. Fibers spun from this critical concentration exhibit theoretically the thinnest skin layer with minimum to no surface defects. Therefore, for comparison reasons, only polyimide, Matrimid 5218, hollow fibers were additionally prepared by using 23 wt. % polymer solution. Polyimide, Matrimid 5218, was purchased from Ciba-Geigy while polyethersulfone, Sumikaexcel, was kindly supplied by Sumitomo. In all cases, *N*-methyl-2-pyrrolidone (NMP, 99% Acros) was used as the polymer solvent and a NMP/H_2O (80/20 wt.%) mixture as the internal coagulant in the hollow-fiber spinning. Finally, polydimethylsiloxane (PDMS; Sylgard-184) commercialized by the Dow Corning Corporation, was used as the rubber-coating material to heal surface defects of the prepared hollow fibers. *n*-Hexane was used as a solvent for the Sylgard-184.

Characterization methods

A Jeol JSM-T220A scanning electron microscope was used to determine the asymmetric structure and the dimensions of the developed hollow fibers. Membrane samples were first immersed in ethanol, fractured in liquid nitrogen and then sputtered with a thin layer of gold using a Balzers Union SCD 040 sputtering apparatus.

The permeation characteristics of the developed hollow-fiber membranes were measured in a high pressure (60 bar) set up by using the variable-pressure method described in Bos et al. (1999) and Kapantaidakis and Koops (2002). For the plasticization of pure gases, the detailed experimental protocol included: (1) thorough degassing and evacuation of the hollow-fiber membranes; (2) determination of pure N_2 and CO_2 permeance and ideal selectivity values at 4 bar; (3) Increase of CO_2 feed pressure from 4 to 18 bar with a step of 2 bar and calculation at each pressure of the CO_2 steady-state permeance; (4) overnight membrane degassing; and (5) iteration of step No. 2. The permselectivity coefficient of the hollow fibers was determined by the ratio of pure CO_2 and N_2 permeance values measured at the same operating conditions. In experiments with the CO_2/N_2 55/45% binary mixture, residue flow rate was kept constant at any feed pressure and equal to 160 NmL/min in order to have relatively low stage-cut values and uniform feed composition across the hollow-fiber modules. Membrane permeate flux determined the total feed flow rate as well as the employed stage cut. In all cases, hollow-fiber membrane modules operated at a countercurrent flow pattern. Feed and permeate compositions were analyzed by means of a Perkin-Elmer Gas Chromatograph equipped with a Porapak Q column. By using feed and permeate compositions and the total gas mixture permeance, the equivalent pure CO_2 and N_2 permeance values were calculated by means of LabView software. The real CO_2/N_2 selectivity was determined by the ratio of CO_2 and N_2 mol fractions in the permeate and feed stream. In order to check the experimental reproducibility, at least two different modules have been tested for each blend composition. The temperature was kept constant and equal to 35°C.

Mathematical modeling

In order to validate theoretically the experimental results obtained, the mathematical model that describes the operation of hollow-fiber membrane permeators was used (Kaldis et al., 1998). In this model the appropriate equations are solved by orthogonal collocation to approximate differential equations, and to solve the resulting system of nonlinear algebraic equations by the Brown method. Compared to other applied computational procedures, this technique minimizes the computational time and improves solution stability.

Results and Discussions

Figure 1 shows the cross section of PES/PI 80/20 (Figure 1a), PES/PI 20/80 (Figure 1b), and PI 100 wt.% (Figure 1c) hollow fibers. In all cases the fibers exhibit a typical asymmetric structure: a dense skin layer supported by a (spongy) porous substructure. A macrovoid free substructure is observed only for PES/PI 20/80 hollow fibers. Figure 2 shows the CO_2 permeance and CO_2/N_2 selectivity of the developed PES/PI and pure PI hollow fibers in comparison with commercial gas-separation membranes. Results refer to PDMS-coated PES/PI and pure PI fibers that have been tested immediately after spinning. PES/PI blends exhibit the highest CO_2/N_2 selectivity (~40) and competitive CO_2 permeance values (40–60 GPU).

Pure PES hollow-fiber membranes have been studied extensively by others, such as Li et al. (1994), Wang et al. (1996), and Chung et al. (1997). For this reason and the fact that this article focuses on polyimide and its blends with PES, pure PES membranes have not been included in this study. For comparison of the permeation performance of similar pure PES hollow-fiber membranes one is referred to Chung et al. (1997). They demonstrated that PES hollow-fiber membranes with a skin layer of about 500 Å can be prepared by using the same approach as we did: one polymer (PES) and one solvent (NMP). Due to the thin skin layer, the prepared membranes exhibited high-permeance values for oxygen (9.3 GPU) and nitrogen (1.6 GPU). It is true that in the specific work the authors did not study the permeation of carbon dioxide. However, this property can be indirectly estimated by using the intrinsic CO_2/N_2 selectivity coefficient of PES dense membranes (Kumazawa et al., 1993). The CO_2/N_2 selectivity coefficient of PES dense membranes is reported to be about 40. Assuming that the same selectivity value can also be achieved for asymmetric PES fibers with a nitrogen perme-

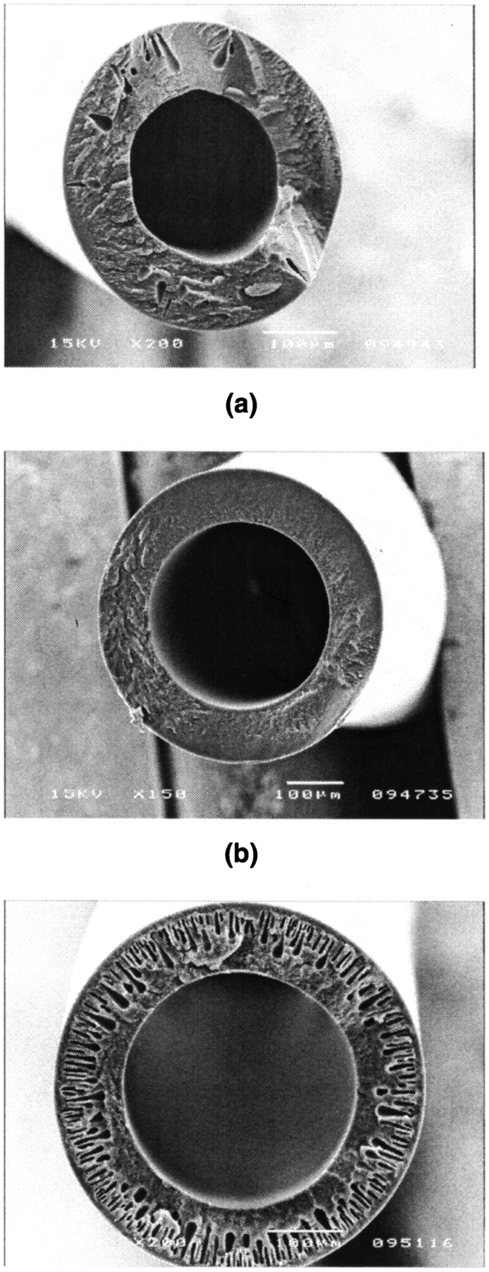

Figure 1. SEM pictures of (a) PES/PI 80/20, (b) PES/PI 20/80, and (c) PI 100%; cross section.

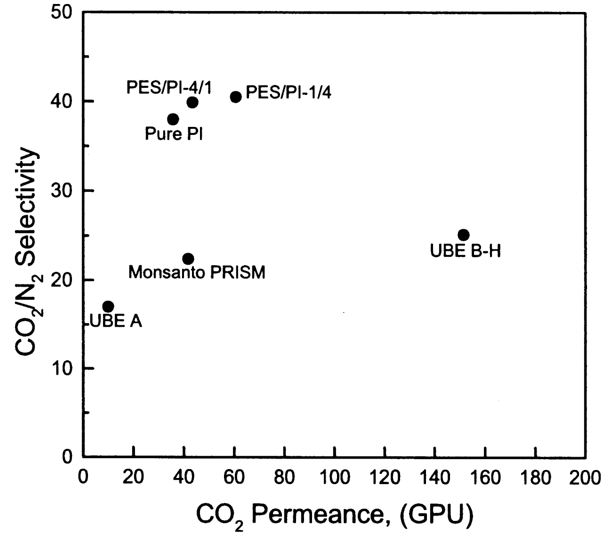

Figure 2. Comparison of PES/PI and PI hollow fibers with commercial gas-separation membranes.

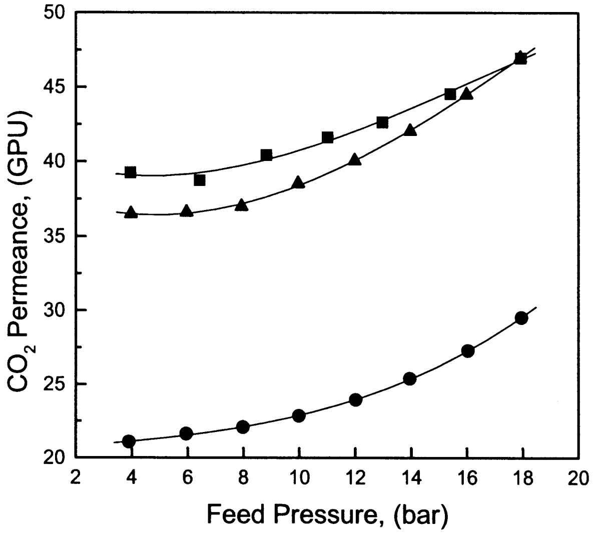

Figure 4. Effect of feed pressure on pure CO_2 permeance.

■: PES/PI 80/20: ▲: PES/PI 20/80; ●: PI 100%.

ance of 1.6 GPU, the CO_2 permeance would be $1.6 \times 40 = 64$ GPU.

Effect of feed pressure on the permeance of pure N_2 and CO_2

Figure 3 shows the effect of feed pressure on N_2 permeance for the three different materials examined in this work. In agreement with the permeation of ideal gases through glassy polymer membranes, the permeance of N_2 is reduced slightly with feed pressure. The thickness of the separating layer δ that corresponds to the specific N_2 permeance values at 4 bar is about 0.13 μm for PES/PI 80/20, 0.12 μm for PES/PI 20/80, and 0.2 μm for PI 100%. Contrary to N_2, the increase of feed pressure results in an increase of the CO_2 permeance, indicating immediate plasticization of the membrane (Figure 4),. Apart from the dependence of CO_2 permeance on feed pressure, the plasticization is evidenced by the reduction of the CO_2/N_2 ideal separation factor (Step 5 of the experimental protocol), which is 11% for PES/PI 80/20, 21% for PES/PI 20/80, and 24% for pure PI. The highest selectivity reduction that is observed for the pure PI hollow-fiber membranes could be attributed to the intrinsic tendency of polyimide membranes to be plasticized at lower CO_2 feed pressures. From the absolute increase of CO_2 permeance it is difficult to compare the magnitude of plasticization for the three different materials. Therefore, the CO_2 permeance at 4-bar feed pressure was used to normalize the permeance. Figure 5 shows that increase of feed pressure results also in higher normalized permeance values, especially for PES/PI 20/80 and pure PI. In Figure 6, an indication of the aging behavior of the three different polymer materials is also given. The reported time period refers to the interval between the permeation measurements for as-spun PDMS-coated hollow fibers and the present series of permeation experiments. PES/PI 80/20 blend hollow fibers exhibit the highest resistance to physical aging.

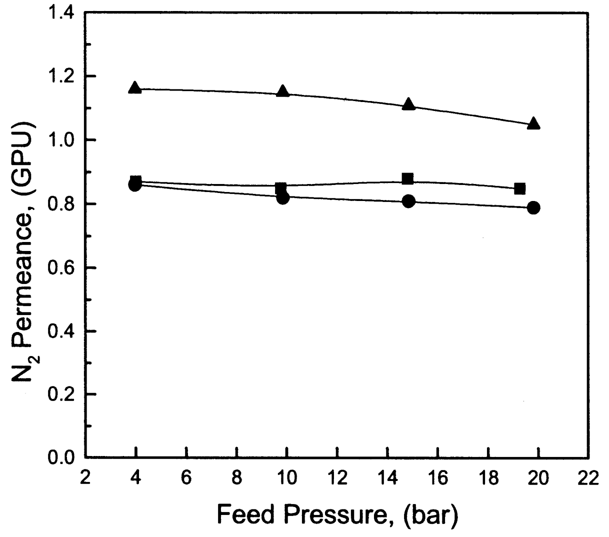

Figure 3. Effect of feed pressure on pure N_2 permeance.

■: PES/PI 80/20; ▲: PES/PI 20/80;●: PI 100%.

A similar CO_2 permeance dependence on pressure also was observed by Ren et al. (2002) in 6FDA-2,6 DAT hollow-fiber membranes. The increase of CO_2 permeance with feed pressure was suppressed by a heat treatment at temperatures between 250 and 320°C. In another work, Wang et al. (2002) studied the CO_2 and CH_4 plasticization of 6FDA-based polyimide hollow fibers. The authors found that an increase of feed pressure from 2.75 bar to 5.5 bar resulted in higher CO_2 permeance values, while an increase of feed pressure from 8.3 bar to 11 bar had almost no impact on the permeance of CH_4.

Pure PI or PES, in the form of dense membranes (20–40 μm), show a typical trend of decreasing permeability with increasing pressure at the low-pressure region (12 and 25 bar,

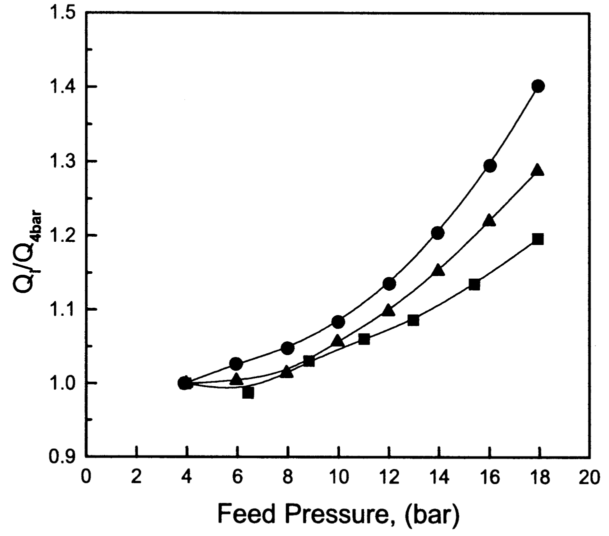

Figure 5. Effect of feed pressure on pure CO_2 normalized permeance.

■: PES/PI 80/20; ▲: PES/PI 20/80; ●: PI 100%.

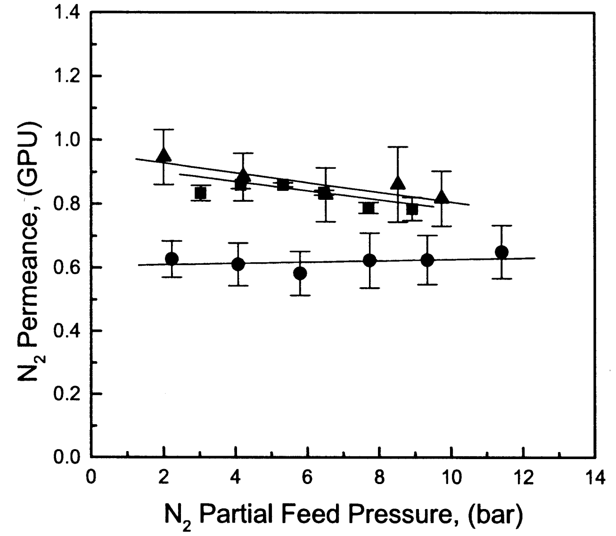

Figure 7. Effect of N_2 feed partial pressure on the N_2 permeance calculated from the mixed-gas experiments.

■: PES/PI 80/20; ▲: PES/PI 20/80; ●: PI 100%.

respectively) and an increasing permeability with a further increase of feed pressure (Bos, 1999; Kapantaidakis et al., 1996). This critical pressure of plasticization was not observed in the case of the PES/PI asymmetric hollow fibers. From the experimental results given earlier and literature references, it can be concluded that the dependence of CO_2 permeance on feed pressure is different between ultrathin asymmetric hollow fibers and the respective dense membranes prepared from the same material. According to Shishatskii et al. (1996), the solubility coefficient of a condensable gas (that is, CO_2) is reversibly proportional to the membrane thickness. As the polymer film becomes thinner, its density increases, the specific volume, V_s, decreases, but the molar cohesion energy, E_{coh}, which is a molecular property of the material, remains constant. Consequently, the cohesive energy density (CED = E_{coh}/V_s) of the material is also increased. A more densely packed glassy material with the same chemical structure would dissolve more gas. Asymmetric (0.1–0.2 μm) hollow fibers could exhibit higher CO_2 sorption capacity and, therefore, accelerated plasticization behavior.

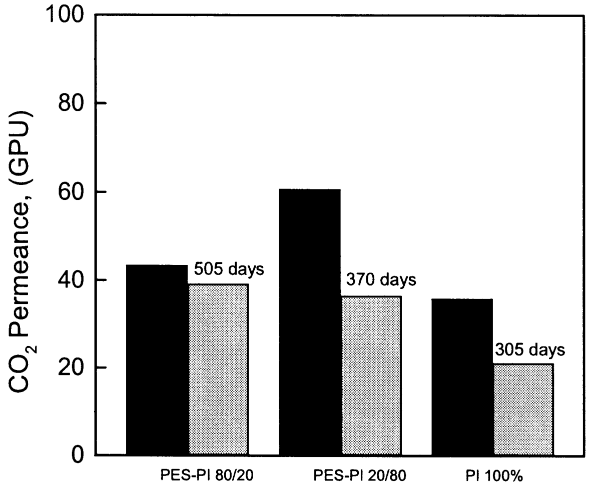

Figure 6. Aging behavior of PES/PI and PI hollow fibers.

Black column: as spun fibers; gray column: aged fibers.

Effect of feed pressure and stage cut on the separation performance of a CO_2/N_2 45/55% binary mixture

Figure 7 shows the effect of N_2 partial feed pressure on N_2 permeance for the three blend compositions. In all cases, an increase of partial feed pressure results in slightly lower (PES/PI 80/20 and 20/80) or constant N_2 permeance (PI 100°) values. Taking into account that the developed ultrathin hollow-fiber membranes showed immediate and pronounced plasticization for pure CO_2 (Figures 4 and 5), one should expect that the permeance of the slower gas (N_2) would also increase with partial feed pressure. However, the permeation behavior of N_2 in the mixture is similar to that reported for the pure-gas experiments (Figure 3), although the absolute values are slightly lower due to physical aging. This is a first indication that both pure PI and PES/PI blend hollow-fiber membranes exhibit entirely different or suppressed plasticization behavior in the permeation of the binary mixture. The latter is also observed in Figure 8 where the effect of CO_2 partial feed pressure on CO_2 permeance is presented. Contrary to the permeation of pure CO_2, the equivalent CO_2 permeance, measured using a CO_2/N_2 mixture, decreases constantly with CO_2 partial feed pressure.

The distinct depression of CO_2 permeance in the binary mixture can be rationalized by considering not only the CO_2 plasticization effect, but also the competition phenomena induced by the coexistence of a second permeating gas, in our

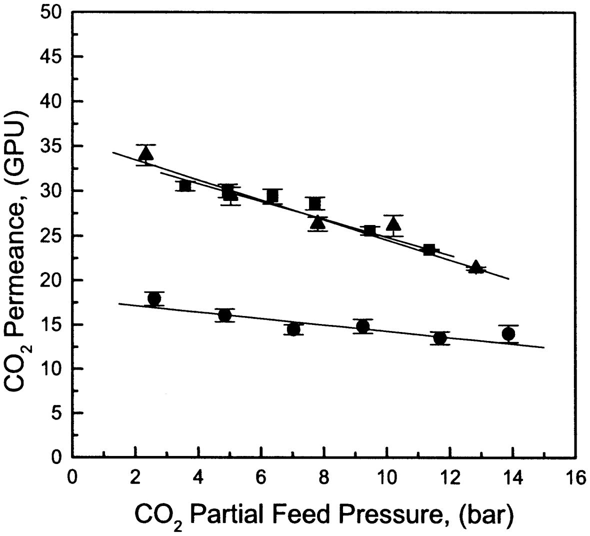

Figure 8. Effect of CO_2 feed partial pressure on the CO_2 permeance calculated from the mixed-gas experiments.

■: PES/PI 80/20; ▲: PES/PI 20/80; ●: PI 100%.

case N_2. The gradual saturation of unrelaxed molecular-scale gaps between polymer chain segments by molecules of two different gases can affect both solubility and diffusivity coefficients. Sanders et al. (1984) reported, for example, the sorption of CO_2, C_2H_4, N_2O, and their binary mixtures in poly(methyl methacrylate). The authors found significant decrements of CO_2 solubility in the mixture relative to the pure-component case at equivalent partial pressures. This competition can result in lower local penetrant concentration, reduced driving-force difference across the membrane, and, therefore, lower gas permeance values (Story and Koros, 1998). From the preceding arguments, it could be assumed that the antiplasticizing effect of a second competing gas would be more intense when its concentration in the mixture becomes higher. In such a work, Donohue et al. (1989) studied the effect of CH_4 mole fraction in CO_2/CH_4 mixtures on the CO_2 permeability of asymmetric cellulose spiral-wound membranes. Indeed, by increasing the content of CH_4 in the feed gas, the CO_2 plasticization was suppressed or even completely eliminated. Therefore, when a minimum CH_4 or N_2 partial feed pressure is exceeded, CO_2 plasticization phenomena are completely offset by competitive sorption effects. The exact critical gas concentrations where this phenomenon occurs in the case of PES/PI blends could be determined by mixed gas sorption experiments, and this work has been scheduled for the forthcoming period.

Figure 9 depicts the dependence of the CO_2/N_2 real selectivity on feed pressure for the three different materials. In absolute values, PES/PI 80/20 fibers exhibit the highest real selectivity coefficients, which vary from 37 to 30. This reduction was completely reversible when the membrane modules were decompressed and tested again at low-pressure levels (such as 4 bar). This is an indication that, over the range of conditions studied, no irreversible swelling of the blend membranes has occurred. In fact, the results suggest that a decreasing selectivity is by no means a proof for plasticization.

An increase of the feed pressure also results in higher stage-cut values and reduced real selectivity coefficients. In our experiments, the total feed pressure varied from 4 bar to 26 bar. By keeping the residue flow rate constant, an increase of pressure resulted in higher permeate flux and, therefore, in stage-cut values increasing from 0.01 to 0.1. In order to evaluate more thoroughly the effect of stage cut on the separation performance of PES/PI 80/20 hollow-fiber membranes, experiments with a varying feed flow rate were carried out at three different stage-cut values for a constant feed pressure of 4 bar. Figure 10 shows that by increasing the membrane stage cut, the permeance of the less permeable component (N_2) increases, while that of CO_2 decreases

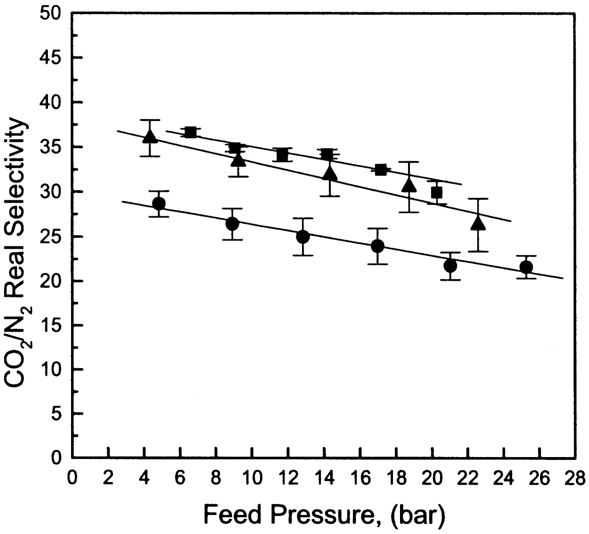

Figure 9. Effect of feed pressure on the CO_2/N_2 real selectivity.

■: PES/PI 80/20; ▲: PES/PI 20/80; ●: PI 100%.

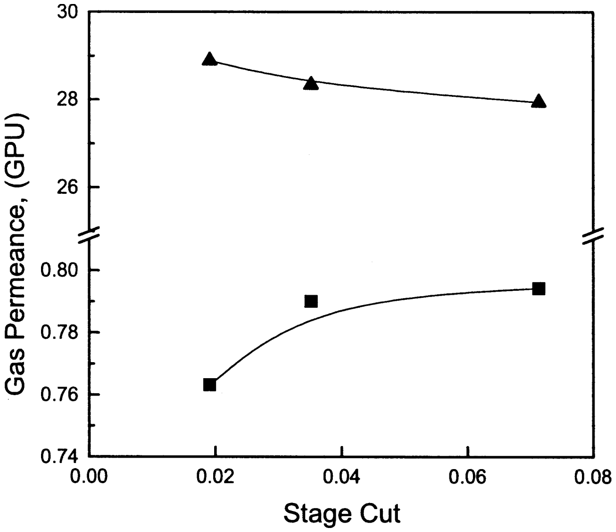

Figure 10. Effect of stage cut on the CO_2 and N_2 permeance calculated from the mixed-gas experiments in PES/PI 80/20 hollow fibers.

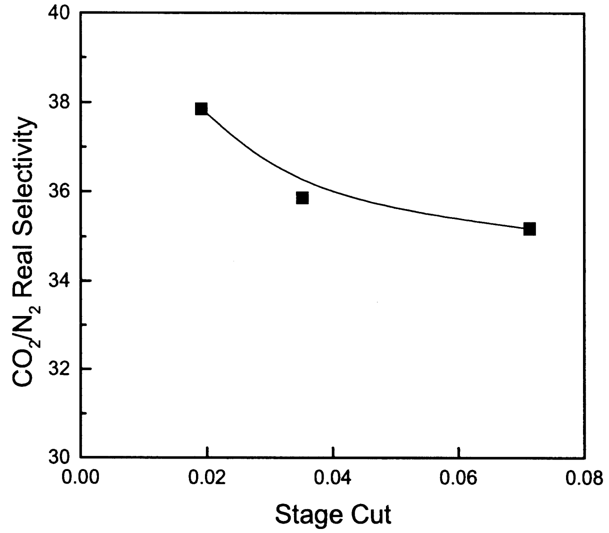

Figure 11. Effect of stage cut on the CO_2/N_2 real selectivity calculated from the mixed-gas experiments in PES/PI 80/20 hollow fibers.

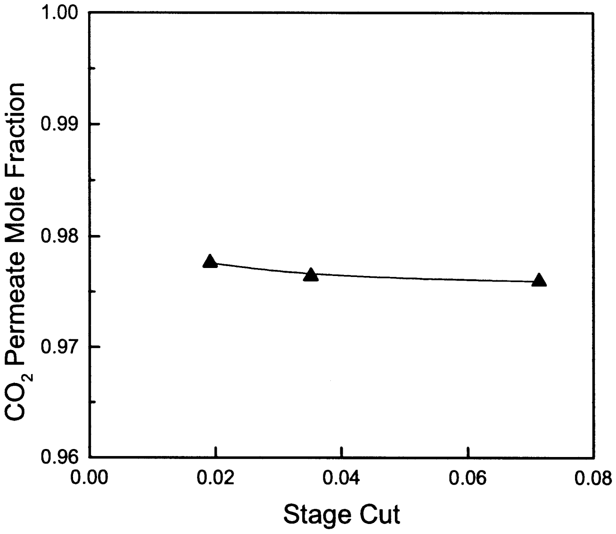

Figure 12. Effect of stage cut on the CO_2 permeate mol fraction calculated from the mixed-gas experiments in PES/PI 80/20 hollow fibers.

slightly. In accordance with previously published results, the lower permeating gas is more sensitive to a variable stage cut (Kaldis et al., 2002). Figures 11 and 12 show the effect of stage cut on the real CO_2/N_2 selectivity values and the CO_2 mole fraction in the permeate stream of PES/PI 80/20 hollow-fiber membranes, respectively. Even for very low absolute values, an increase of stage cut from 0.02 to 0.07 results in a 7% reduction of the real selectivity coefficient, while the CO_2 concentration in the permeate stream remains almost constant.

Comparison between experimental data and simulation results

In order to validate the obtained experimental results the mathematical model developed by Kaldis et al. (1998) was used. The input data to the model were the geometrical characteristics of the membranes (outer/inner diameter, length, and number of fibers), the feed properties (composition, flow rate), and the main process variables (pressure and temperature). Two different cases were examined: (1) permeance values, obtained from pure gas experiments at 4-bar feed pressure, and (2) permeance values, obtained from the separation of the CO_2/N_2 binary mixture at different feed pressures. The output data of the model were the permeate flow rate and the gas compositions of permeate and residue streams. Concentration and flow-rate gradients along the hollow fibers in both the feed and permeate streams could also be estimated. Figures 13a–13b show the comparison between experimental points and simulation trials in terms of stage cut for PES/PI 80/20 (Figure 13a), PES/PI 20/80 (Figure 13b), and PI (Figure 13c) hollow fibers. In the first case, where the gas permeance values are considered constant and pressure independent, the membrane separation performance is clearly overestimated. The simulated stage-cut values are higher than the experimental ones, especially in the high-pressure region. This deviation from real conditions would be even higher if the mathematical model incorporated the dependence of gas permeance on feed pressure, as obtained in the experiments for pure gases (Figures 3 and 4). Since the pure CO_2 permeance increases with feed pressure, the ideal CO_2/N_2 selectivity factor would also increase, resulting in very high stage-cut values and permeate purities. In the second case, where the experimental gas permeance values, obtained from the separation of the binary mixture, are used in the mathematical model, the simulated stage-cut values are in excellent agreement with the experimental points. Respectively, Figures 14a–14c show the comparison between experimental results and simulation predictions in terms of CO_2 permeate mole fraction for PES/PI 80/20 Figure (14a), PES/PI 20/80 (Figure 14b), and PI (Figure 14c) hollow fibers. In all cases, the relative deviation varies between 0.3 and 1.4%. Similar permeate purity values were obtained by using the mathematical model proposed by Weller and Steiner (1950). This model can be easily applied to small modules in which the complete mixing case can be considered. Table 1 compares the experimental CO_2 mole fractions measured in PES/PI 80/20 hollow fibers with the predictions of Kaldis and Weller–Steiner models, by taking into account pressure-independent permeance values. The results are quite comparable, which means that the separation performance is insensitive to the applied flow conditions inside the PES/PI modules.

From the preceding discussion, the importance of studying the performance of polymer membranes in conditions comparable to real industrial applications (ultrathin asymmetric hollow fibers, high-pressure operation, multicomponent, or at least binary mixtures) is clearly depicted. Apart from previously studied properties, such as glass transition temperature, solubility and diffusivity coefficients, and aging, it is proven that ultrathin (0.1–0.2 μm) asymmetric membranes show different CO_2 plasticization behavior. Increase of feed pressure results in an immediate increase of CO_2 permeance and subsequent reduction of the ideal CO_2/N_2 selectivity. However, this accelerated plasticization tendency is not as pronounced

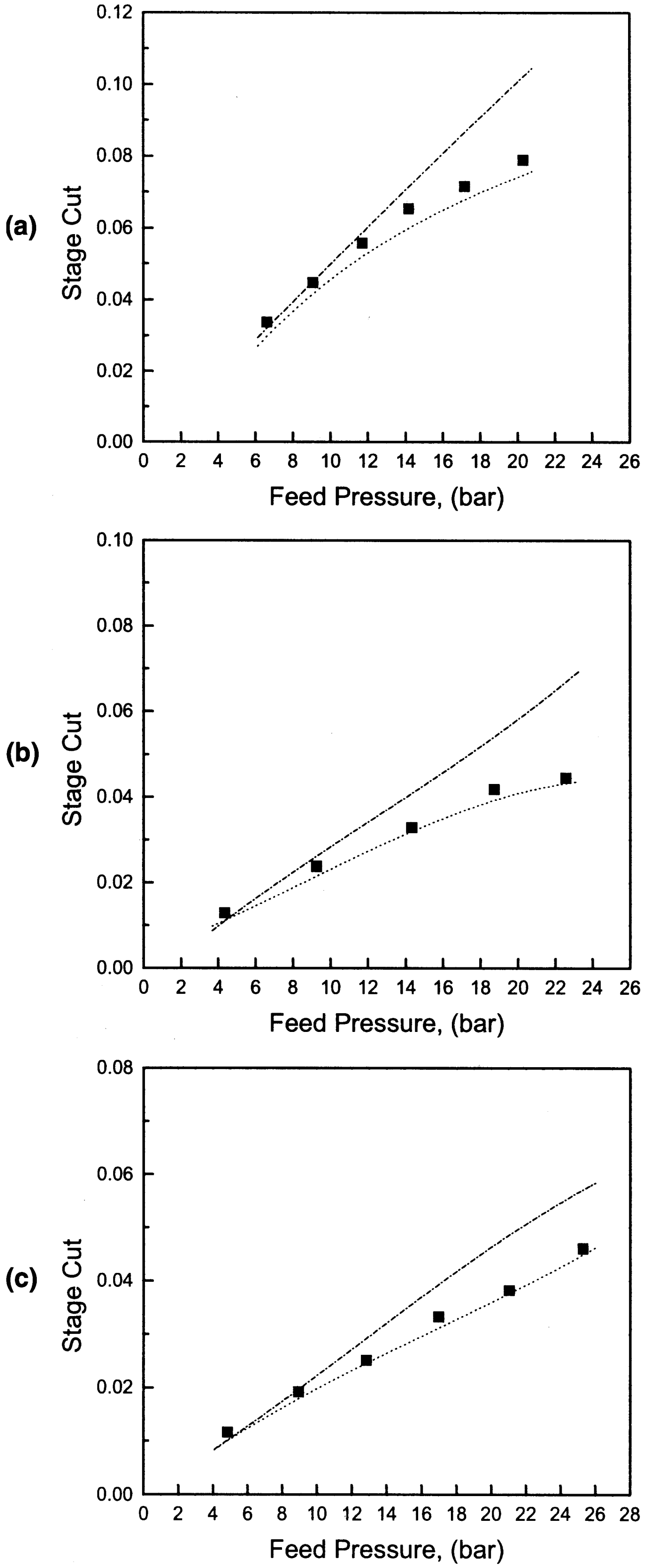

Figure 13. (a–c) Effect of feed pressure on stage cut for PES/PI 80/20 (13a), PES/PI 20/80 (13b), PI 100% (13c) hollow fiber membranes.

■: experimental results, dash dot line: simulation results for constant permeance, dot line: simulation results for pressure dependent permeance.

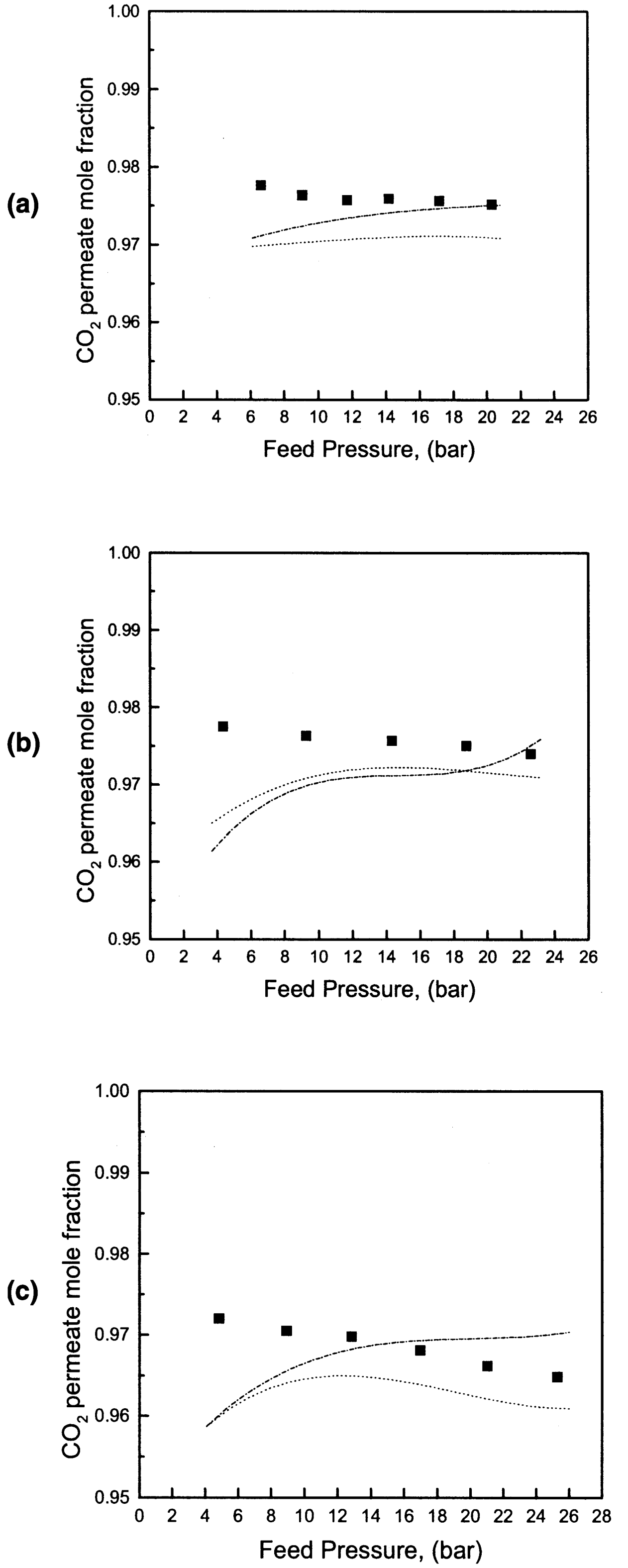

Figure 14. (a–c) Effect of feed pressure on permeate purity for PES/PI 80/20 (14a), PES/PI 20/80 (14b), PI 100% (14c) hollow fiber membranes.

■: experimental results, dash dot line: simulation results for constant permeance, dot line: simulation results for pressure dependent permeance.

Table 1. Comparison Between Experimental CO_2 Permeate Mole Fractions and Simulation Predictions by Weller–Steiner and Kaldis Models

Pres. (bar)	CO_2 Permeate Mole Fraction, Exp.	CO_2 Permeate Mole Fraction, Weller–Steiner Model	CO_2 Permeate Mole Fraction, Kaldis Model
6.6	0.977	0.978	0.972
11.7	0.976	0.978	0.974
20.3	0.974	0.98	0.976

when a CO_2/N_2 55/45% binary mixture is fed to the PES/PI blend hollow fibers. Competition phenomena from the slower permeating gas, N_2, reduce the sorption of CO_2 and the magnitude of membrane swelling. Furthermore, process variables such as feed pressure, feed flow rate, and stage cut can also affect the separation performance of the hollow-fiber membranes. From the three different membranes examined in this work, PES/PI 80/20, PES/PI 20/80, and PI 100 wt. %, it is not clear if the utilization of the high-cost engineering polyimide offers any significant improvement compared with the traditional type of polyethersulfone. To the contrary, membranes prepared from pure PI suffered from the most severe aging phenomena. Whether the higher aging resistance of PES/PI blends is due to the intrinsic endurance of pure PES or to specific chemical interactions between the two miscible components remains a speculation, in the absence of permeation data of pure PES hollow-fiber membranes. For the specific separation task (CO_2/N_2), the traditional glassy polymer of polyethersulfone competes directly with the novel engineering polyimide, Matrimid 5218, in terms of stability, cost, and separation performance.

Conclusions

Ultrathin (0.1–0.2 μm) asymmetric hollow fibers based on polyimide and polyethersulfone/polyimide blends show accelerated pure CO_2 plasticization phenomena and subsequent reduction of the ideal CO_2/N_2 permselectivity. However, in the case of CO_2/N_2 binary mixture permeation, the plasticization behavior is suppressed due to competitive sorption of N_2. Separation results have been validated by means of a computer model algorithm simulating the operation of asymmetric hollow-fiber membranes. Experimental results and simulation predictions are in very good agreement only when gas permeances calculated from the separation of the CO_2/N_2 mixture are introduced in the model. The reported separation performance and the resistance to physical aging establish polyethersulfone/polyimide blends as excellent candidate membrane materials for the separation of gaseous mixtures at the industrial level.

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