Suppression of Gas Separation Membrane Plasticization by Homogeneous Polymer Blending

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Plasticization is a phenomenon frequently encountered in the application of glassy polymeric materials for solution–diffusion membranes. Conventional methods for stabilizing the membrane are either annealing or cross-linking, which hardly influence the selectivity of the membrane, but decrease the permeability. For single-gas experiments, the literature shows that plasticization can be stabilized by blending a polymer with high plasticization tendencies with one that is hardly affected by the sorbed molecules. Most permeation experiments are carried out with pure CO_2, but little is known about the transport properties determined from mixed gas experiments. Stabilization of plasticization in mixed-gas experiments for polymer blends of the polyimide Matrimid and polysulfone is reported, as well as transport properties of a new homogeneous polymer blend based on Matrimid and the copolyimide P84. Experimental results show that the material is stabilized against carbon dioxide plasticization and selectivity for a carbon dioxide/methane mixture significantly improves.

Introduction

Gas separation processes based on glassy solution-diffusion membranes frequently suffer from plasticization of the stiff polymer matrix by the sorbed penetrant molecules (Chiou et al., 1985; Wessling et al., 1991, 1995; Chern and Provan, 1991; Ilinich and Zamaraev, 1993; Ilinich et al., 1995; White et al., 1995; Okamoto et al., 1997). Bos et al. (1999, 1998a,b) investigated the mechanism of CO_2-induced plasticization, chemical and physical treatment of the polymer to prevent plasticization, and estimation of the impact of membrane stabilization on the economics of a gas separation process. This article focuses on the suppression of plasticization by polymer blending.

Polymer blending is a possibility of modifying material properties. A blend can show new properties not found for single polymers. This also holds for membrane preparation to tailor a specific separation performance. For instance, Ube prepared membranes from BPDA-based polyimide blends (Nakamura, 1989). Furthermore, blending is an option for reducing the price of the membranes. Considering the polyimide Matrimid in particular, several examples can be found in the patent literature where membranes are prepared from Matrimid and the much cheaper PEI (Simmens and Ikiner, 1993; Macheras et al., 1995).

It is well known that many polymers do not mix on a molecular level. The blends contain the separate polymers as individual domains or phases (Camargo et al., 1991). Blends often consist of a matrix of one polymer containing another polymer as a dispersed or cocontinuous phase. The polyimide Matrimid, however, can be blended on a molecular level with PC (Camargo et al., 1991), PSF (Camargo et al., 1991; Kapantaidakis et al., 1996), PES (Grobelny et al., 1990; Liang et al., 1992; Guerra et al., 1988, Cha et al., 1994). and polybenzimidazole (PBI) (Kapantaidakis, 1999). Blending on a molecular level, for example, is indicated by a single glass transition temperature and the optical transparency of the films.

In single-gas CO_2 permeation experiments, Kapantaidakis et al. (1999) showed that the plasticization pressure of the polyimide Matrimid was shifted toward higher feed pressures by blending it with polysulfone, a polymer with a significantly higher plasticization pressure than Matrimid. However, their article does not indicate whether this apparent stabilization indeed translates into a stabilization of the slower permeating methane, as can be determined by mixed-gas experiments.

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In the following we will demonstrate that

- Homogeneous blending not only stabilizes the single-gas permeation properties of a polymer but also avoids the increased product loss of mixed-gas experiments.
- Homogeneous blending of the polyimide Matrimid and polysulfone (equally by weight) results in improved plasticization behavior, but spoiled permeation and separation performance.
- Blending the polyimide Matrimid with a copolyimide P84 (60/40) stabilizes the polymer against plasticization while simultaneously improving the separation performance.

Experimental Studies

Film preparation

Polysulfone Udel P3500 (PSF) was supplied by Amoco: P84 (copolyimide of 3,3′4,4′-benzophenone tetracarboxylic dianhydride and 80% methylphenylene-diamine + 20% methylene diamine) was obtained from Lenzing; and Matrimid 5218 (polyimide of 3,3′4,4′-benzophenone tetracarboxylic dianhydride and diamino-phenylindane) came from Ciba-Geigy. Film preparation of the pure polymers is described in detail in Bos et al. (1999). A 10% Matrimid/PSF (50/50) wt. %) in $CHCl_3$ solution and a 20% Matrimid/P84 (60/40 wt. %) in DMAc solution were cast on a glass plate and dried in a nitrogen atmosphere at room temperature. The dried films were removed from the glass plate with a small amount of water and dried further in a vacuum oven (Heraeus, RVT 220/180) at 150°C for at least four days. The final film thickness was 18 μm for the Matrimid/PSF and 27 μm for the Matrimid/P84 blend.

Characterization Methods

The experimental methods to determine the single- and mixed-gas permeation properties are described in detail in Bos et al., (1999). This article also explains in detail the influence of temperature and casting solvent on the plasticization behavior in single-gas experiments. Wessling et al. (1991) describes a two-cell sorption setup that allows the measurement of the sorption as well as the diffusion coefficient. Therefore, values of gas concentrations in the polymer as well as diffusion coefficients are derived directly from sorption experiments, but they are not extracted from permeation experiments. For mixed-gas permeation experiments, the composition of the mixed gas was adjusted to cover the same range of feed pressures as was used in single-gas experiments, to allow comparison of mixed- and single-gas experiments.

Table 1. Glass Transition Temperature and Densities of Polymers and Polymer Blends Used in Gas Permeation Experiments*

Polymer	Solvent	Density (g/cm^3)	Glass Transition Temp. (°C)
Matrimid	DMAc	1.229	313
60%M/40%P84	DMAc	1.288	307
P84	DMAc	1.336	300
Matrimid	DMAc	1.229	313
50%M/50%PSF	$CHCl_3$	1.221	191 and 319
PSF	NMP	1.236	182

*Glass transition temperatures are determined from a second heating run.

Glass transition temperatures of the polymer films are determined on a Perkin-Elmer DSC-7 calorimeter with a heating rate of 30°C/min. In most cases, no transitions were observed in the first heating run. The glass transition temperatures were therefore taken from the second run. The average glass transition temperature, determined from two samples prepared from the same cast film, has a standard deviation of ±1°C.

Results and Discussion

Membrane properties

The glass transition temperatures and the densities of the homopolymers and their blends are summarized in Table 1. The casting solvents used are also given, as they may influence the results to a certain extent. In general, the magnitude of the permeability can vary; however, the general phenomenon of membrane plasticization, as well as the plasticization pressure, is not influenced by the choice of the casting solvent (Bos et al., 1999). The densities of the different films varied from 1.221 g/cm^3 for the Matrimid/PSF blend to 1.336 g/cm^3 for P84. The density of the Matrimid/P84 blend falls between the values of the homopolymers. The density of the Matrimid/PSF blend is lower compared to the homopolymers. This may be explained by the casting solvent used. The films prepared from the homopolymers were cast from DMAc, whereas the blend was cast from the more volatile $CHCl_3$. A film cast from $CHCl_3$ will dry faster compared to a film cast from DMAc. In the case of the $CHCl_3$ cast film, the polymer chains have less time to relax into a dense packing, as in the case of the DMAc cast film, which results in a lower density for the $CHCl_3$ cast film.

The blends, Matrimid/P84 and Matrimid/PSF, were transparent. The Matrimid/PSF blend appears to have two glass transition temperatures, indicating therefore a phase-separated blend morphology. However, this interpretation is not valid: the glass transition temperatures for the Matrimid/PSF blend are taken from the second DSC run. During the first run, the sample was heated well above the glass transition temperature of the polyimide. From the recent literature (Kapandaidakis et al., 1999) on the phase behavior of Matrimid/PSF blends, one must conclude that the phase separation stems from the first heating run. Optical clarity is not a sufficient measure for determining blend homogeneity. For example, thin films of heterogeneous blends appear clear, as the light encounters only one of the two phases in passing through the material (MacKnight et al., 1978). Furthermore, the two polymers can have equal refractive indices or the dispersed phase has dimensions smaller than the wavelength of the visible light (MacKnight et al., 1978). Based on these arguments, we conclude that the Matrimid/PSF blend to be homogeneous before the DSC experiment and during transport characterization. For the Matrimid/P84 blend we observed one single-glass transition temperature even during the second run and assume this blend to be homogeneous as well.

Single-gas permeation properties of Matrimid/P84 blend

Single-gas permeation together with sorption experiments are only carried out with the Matrimid/P84 blend since the properties of Matrimid/PSF blend are extensively reported in (Kapantaidakis et al., 1996). Figure 1 shows the CO_2 per-

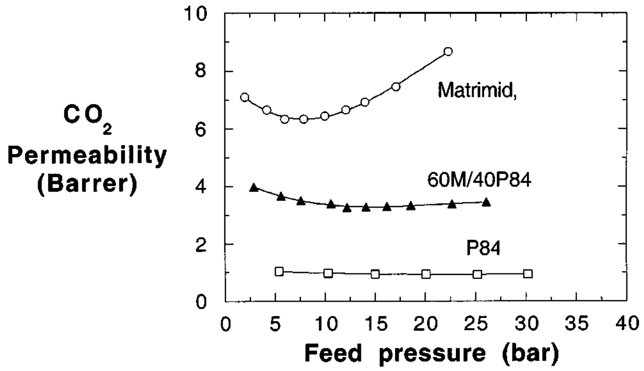

Figure 1. CO$_2$ permeability as a function of pressure for Matrimid, a Matrimid/P84 blend (60/40) wt. %), and P84 at room temperature (23–24°C).

meation behavior of the blend in comparison with the homopolymers at room temperature. The permeability coefficients of the blend are found between the values of the homopolymers. On the basis of the film densities it can be concluded that blending Matrimid with P84 results in a densification of the polymer matrix, and hence a reduction of free volume. The densification of the polymer matrix results in lower permeability values. Compared to P84 the blend has a larger free volume, and therefore a higher permeability. Similar results are found in the literature for polystyrene/poly(phenylene oxide) (PS/PPO) (Morel and Paul, 1987), and polystyrene/polymethylmethacrylate (PS/PMMA) blends (Raymond et al., 1993). The permeabilities of these blends also fall between the values of the homopolymers.

The plasticization pressure of the Matrimid/P84 blend is shifted to higher feed pressures. The blend shows a plasticization pressure of 15 bar, which is between the plasticization pressure of 9 bar found for the Matrimid film and the 22 bar found for the P84 film (Bos et al., 1999). Kapantaidakis et al. (1996) found a similar shift in plasticization pressure for a Matrimid/PSF blend. The plasticization pressure of the blend shifted to higher pressures with increasing PSF content. Furthermore, only a slight increase in permeability of the Matrimid/P84 blend is observed at pressures above the plasticization pressure. Hence, blending of 60% Matrimid and 40% P84 does not completely suppress plasticization at room temperature. The reason that the CO$_2$-plasticization is not completely suppressed as Matrimid is blended with P84 may be attributed to the concentration of P84 in the blend. The blend consists of only 40% P84 and is expected to be more like Matrimid than P84.

Sorption and diffusion properties

Using a pressure-decay method, gas solubility as well as diffusivity belonging to that concentration can be measured as described by Wessling et al. (1991). For the Matrimid/P84 blend and the two homopolymers the sorption isotherms and the average diffusion coefficient were determined, as a function of concentration, to further characterize pure polymers and their blend. Figure 2 gives the sorption isotherm and Figure 3 the concentration-dependent diffusion coefficient. The CO$_2$ concentration in the P84 film is lower than in the Matrimid/P84 and Matrimid film at corresponding pressures. The sorption isotherms of Matrimid and the blend are comparable. It is not clear why the sorption isotherms of the Matrimid film and the blend coincide. The sorption isotherm of the blend was expected to be between the isotherms of the homopolymers (MacKnight et al., 1982). The diffusion coefficients of the blend correspond with the diffusion coefficients of P84, which is lower compared to Matrimid. This explains the lower permeability of the blend compared to Matrimid, as the concentration in the blend is comparable to Matrimid. Hence, Matrimid blended with P84 results in a decrease in diffusivity.

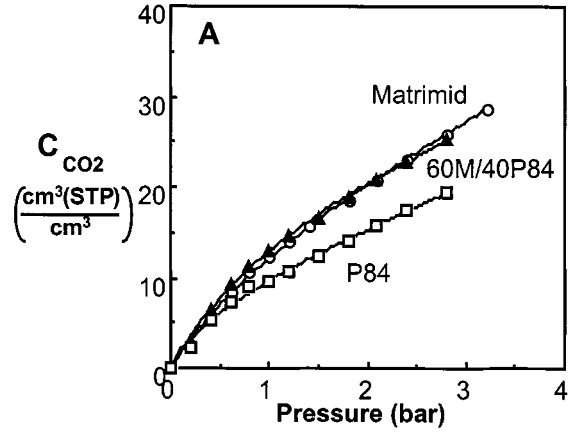

Figure 2. Sorption of CO$_2$ for the Matrimid/P84 blend and the homopolymers at 35°C.

CO$_2$/CH$_4$ mixed-gas permeation behavior

Mixed-gas permeation experiments were carried out for the 60% Matrimid/40% P84 and 50% Matrimid/50% PSF blends, as well as for the pure Matrimid membrane. Figure 4 shows the CO$_2$/CH$_4$ selectivity obtained with a 55/45 mol % CO$_2$/CH$_4$ mixture as a function of the total feed pressure for both blends and the homopolymers Matrimid and PSF.

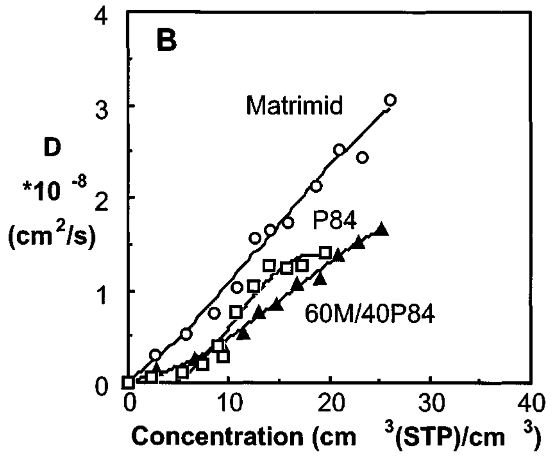

Figure 3. Average diffusion coefficients of CO$_2$ for the Matrimid/P84 blend and homopolymers at 35°C.

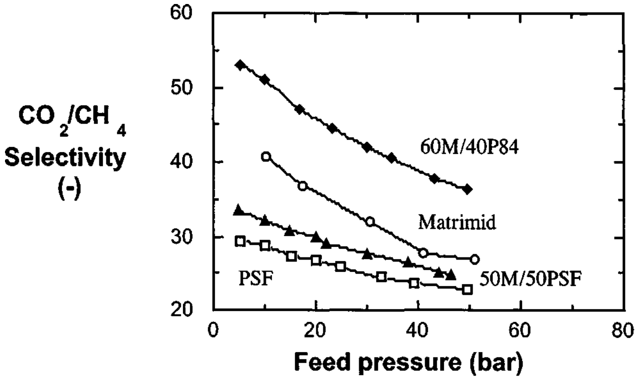

Figure 4. CO_2/CH_4 selectivity as a function of total feed pressure of the Matrimid/P84 and Matrimid/PSF blends, and the homopolymer Matrimid obtained with a 55/45 mol % CO_2/CH_4 mixture at 35°C.

The selectivity of P84 was not measured because of the very low fluxes and high selectivity. Measurement of the small CH_4 concentration in CO_2 was limited by the gas chromatographic detection method used. But to give an indication of the magnitude of the selectivity of P84, an ideal selectivity of 89 was measured at 5 bar and 25°C.

The selectivities of the blends fall between the values of the homopolymers. Raymond et al. (1993) report similar trends for the selectivities of the PS/PMMA blends. The selectivity of PMMA was the highest and decreased with increasing PS concentration. The striking feature of Figure 4 is the significant increase in selectivity when Matrimid is blended with P84. Blending with PSF only decreases the selectivity. Earlier identified methods such as annealing (Bos et al., 1998b) and cross-linking by interpenetrating networks (Bos et al., 1998a) prevent plasticization but hardly affect the selectivity.

Furthermore, one observes in Figure 4 that the selectivity decreases with increasing feed pressure. However, one must not draw conclusions from such selectivity trends in the plasticization behavior. Below the plasticization pressure, both CO_2 and CH_4 permeability show a decreasing permeability with increasing feed pressure. However, CO_2 generally has larger decreases than CH_4, resulting in decreasing selectivity. Therefore, the permeability of CO_2 as well as CH_4 must be plotted as a function of the partial feed pressure. Such permeation isotherms are given in Figures 5 and 6.

The total permeability curve of the Matrimid/PSF blend falls between the permeability curves of the homopolymers. This was in fact, expected from results in earlier published literature (Morel and Paul, 1982; Raymond et al., 1993); however, it is not clear on the basis of the densities of the films. The same behavior is observed for the partial CO_2 permeation curve of the blend. The shape of this curve is similar to the curve of PSF. The permeability does not increase at higher feed pressures, suggesting a suppression of plasticization. However, the partial CH_4 permeability of the blend still shows a slight increase (~ 5%) with increasing feed pressure. Considering the estimated error in the permeability measurement of 4 to 10% (being larger at lower pressures), the increase in CH_4 permeability may not be significant.

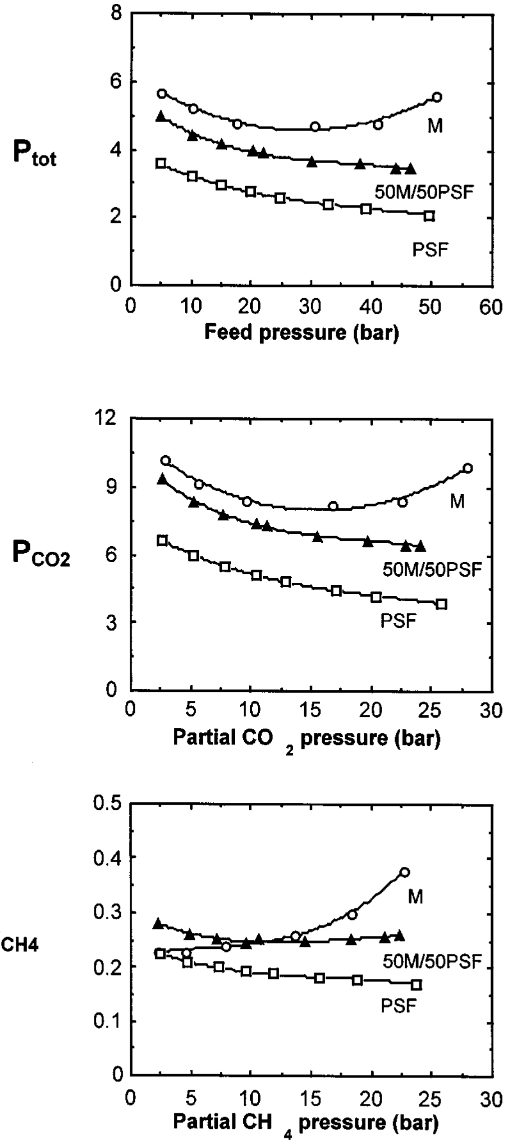

Figure 5. Permeability-pressure curves obtained with a 55/45 mol % CO_2/CH_4 mixture at 35°C for the Matrimid/PSF and the homopolymers Matrimid (M) and PSF.

The permeabilities are given in Barrer.

From the Matrimid/P84 blend shown in Figure 6, we see there is no increase in the total permeability and the partial CO_2 permeability at elevated pressures, demonstrating that the polymer has been stabilized against plasticization. The values for the CO_2 permeability obtained in the mixed-gas permeation experiment compare well with the data obtained in the single-gas experiment reported in Figure 1. The slight minimum observed in the single-gas experiment is not found in Figure 5. This, however, falls within the experimental error of the permeation method (Bos et al., 1999). The CH_4 permeability still shows an increase of about 20%, indicating a small tendency to plasticize, and agrees with the minimum of the CO_2 permeability in Figure 1.

From the preceding experimental findings, one can conclude that the transport properties of the polyimide Matrimid

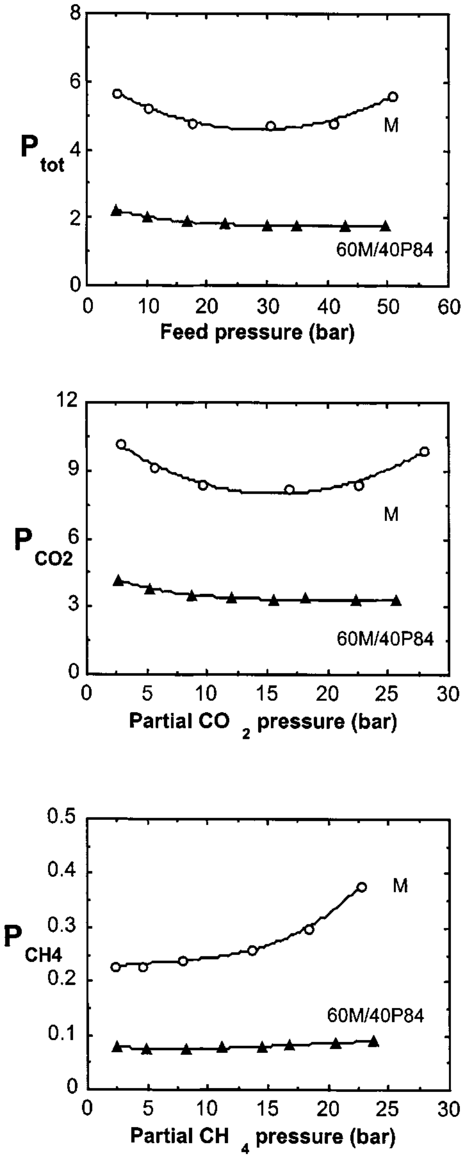

Figure 6. Permeability-pressure curves obtained with a 55/45 mol % CO_2/CH_4 mixture at 35°C for the Matrimid/P84 blend and the homopolymer Matrimid (M).

The permeabilities are given in Barrer.

can be tailored by homogeneous blending with other glassy polymers, such as polysulfone or the copolyimide P84. It is currently not known, however, how the suppression of plasticization quantitatively correlates to the composition of the two blends. The questions whether the observed behavior also holds for phase-separated blends remains open and requires further extensive experimental effort. Indeed, recent literature (Kapantaidakis et al., 1999) indicates that the permeation behavior of He through Matrimid/PSF-blend membranes strongly depends on the composition and the thermal history of the membrane. Kapantaidakis et al. conclude that the transport in a phase-separated Matrimid/PSF is dominated by the polyimide over a wide concentration range. Assuming that the plasticization behavior may also be dominated by the polyimide, one has to conclude that only the homogeneous blend is less susceptible to plasticization. With respect to industrial membrane development, one may then wonder whether the choice of a blend that may phase separate upon heat treatment is justified. A polymer blend such as Matrimid/P84 would be advantageous, since it is characterized by a much larger miscibility/temperature window. Still these conclusions remain speculation until an extensive study on the extent of plasticization as a function of blend composition and blend morphology is carried out for both blends.

Conclusions

Blending of a polymer that is highly susceptible to plasticization with a polymer that hardly plasticizes presents a simple method to suppress plasticization. Stabilization against plasticization can be obtained by a polymer such as PSF resulting in a decreasing selectivity. The proper tailoring of the blend to (1) stabilize the membrane against plasticization, and (2) increase the selectivity by a slight relaxation in permeability was successfully demonstrated by blending the polyimide Matrimid with the copolyimide P84.

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