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Physical aging and carbon dioxide plasticization of thin polyimide films in mixed gas permeation



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ABSTRACT

The gas permeation properties from thick (bulk) films have long been used as a guide to the performance of asymmetric membranes with a very thin selective skin (~100 nm). However, recent research has shown that thin films of glassy polymer with a similar thickness undergo more rapid physical aging than such thick films, leading to different permeation characteristics. Our prior work has dealt with pure gases, and most recently, pure CO₂ has been used to explore the difference in plasticization behavior for thick and thin films. This paper is the first effort to look at mixed gases involving CO₂ and how thin films differ from thick films. Thick and thin films made of Matrimid, an important polyimide for commercial gas separation membranes, have been investigated by monitoring their gas permeability and selectivity simultaneously for CO₂/CH₄ and CO₂/N₂ gas mixtures. The effects of film thickness, aging time, pressure, gas pair and gas composition on mixed gas behavior have been discussed in detail. The pressure dependence of pure gas permeability has also been measured as a control. Matrimid films become more vulnerable to CO₂ plasticization as the thickness is reduced to the range of thin selective skins of asymmetric membranes and with increasing aging time. Competitive sorption/permeation effects appear to be more pronounced and the combined effect of CO₂ plasticization and competitive sorption/permeation on thin Matrimid films seems to be more severe for CO₂/CH₄ feed mixtures than for CO₂/N₂ mixtures.

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1. Introduction

The invention of asymmetric membranes, comprised of an ultra-thin layer of dense polymer (~100 nm) overlaying a porous support, by Leob and Sourirajan in the 1960s [1] for water desalination was also a first step towards practical membranes for other applications like gas separations. Conversion of the asymmetric structure to a hollow fiber form based on bisphenol-A polysulfone plus the addition of a silicon rubber coating to caulk defects led to the initial commercial use of membranes for gas separations [2,3]. Since the introduction of polysulfone as a gas separation membrane material, thousands of other glassy polymers have been screened for this use by evaluating their pure gas permeability in the form of thick dense films [4]. Few have been investigated by measuring mixed gas permeation behavior [5–11], and even fewer have been fabricated into hollow fibers and tested with mixed gases [12–20] because this involves a great deal of cost and time plus a series of skills available in only a few laboratories.

Recent studies on free-standing thin films of glassy polymers suggest that thick film data may not give a full picture of the material's performance when in the form of a practical high flux membrane, since the pure gas permeability of these thin films have been found to be a function of thickness and time for glassy polymers [21–35]. This thickness and time effect may be especially critical for polymers with an ultra-high free volume.

The excess free volume of glassy polymers that results from their non-equilibrium nature leads to physical aging, or densification, that reduces their free volume over time [36,37]. This process happens more rapidly as the thickness of the film decreases apparently owing to the higher segment mobility in the proximity of a free surface [38]. As a result of this physical aging process, the pure gas permeability decreases with aging time. It is the same non-equilibrium character that causes gas sorption isotherms in glassy polymers to be concave to the pressure axis, which is well described by the so-called “dual-mode sorption” model [39]. As a result, the apparent, or secant solubility coefficients decrease as the gas pressure increases. The permeability coefficient, which is a combination of solubility and diffusivity behavior, also decreases with increasing upstream pressure in the absence of plasticization and can be described by an analogous “dual mobility” model. Such behavior has been extensively reported for a variety of glassy

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polymers in the form of thick dense films. However, similar reports for thin films or hollow fibers are much more limited but there is much evidence that thin films behave differently than thick films, including the process of plasticization by highly soluble gases like CO₂. Horn and Paul [39] systematically compared the pressure dependence of the permeability of CO₂ for thick and thin Matrimid films and found that thin films were more prone to plasticization by CO₂ than thick films.

To date, the differences between the permeation behavior of thick and thin films have been limited to observations using pure gases [33]. It is the objective of this paper to explore the difference in thick and thin film behavior using mixed gases since this is the ultimate test of performance in an actual separation process. This work uses the polyimide known as Matrimid since it is an important material for commercial gas separation membranes. A main focus of this work is on the plasticization of Matrimid by CO₂ in the feed mixtures when the other gas in the binary mixtures is either CH₄ or N₂ since these gas pairs relate to some important applications, such as natural gas purification and CO₂ capture in flue gases. Prior work has shown that the permeability of thin films that have been heated above the polymer glass transition temperature (T_g) age very rapidly in the first tens of hours following cooling to the measurement temperature. This aspect is not the focus of the current work but rather the mixed gas behavior after the films have aged for times that get beyond this period of initial rapid change. Thus, all films used in this work have been aged for 100 h or more prior to any measurements.

2. Experimental

2.1. Film preparation

The commercially produced polyimide, 3,3'-4,4'-benzophenone tetracarboxylic-dianhydride diaminophenylindane (BTDA-DAPI), commonly known as Matrimid 5218 (Huntsman Chemical), was investigated in the form of thin and thick films, due to its importance as an industrial separation membrane material. The glass transition temperature (T_g) of this polymer is reported to be 310 °C [33].

Thick films were cast from a filtered 3.0 wt% Matrimid/dichloromethane (Fisher Scientific, AR grade) solution in metal casting rings on silicon wafers. Freestanding, single-layer thin films were made by spin casting 4.0 wt% Matrimid/cyclohexanone (Sigma-Aldrich, AR grade) solutions onto silicon wafers. The solution was filtered through 0.45, 0.2 and 0.1 μm PTFE membranes in order to remove any particles that would lead to defects. The thickness was controlled by varying the polymer solution concentration and spinning speed as described in detail elsewhere [24]. A variable angle spectroscopic ellipsometer (J.A. Woollam Co., V-VASE[®]) was used to determine the thickness of the thin films [26].

In order to mitigate the effect of possible pin hole defects and to provide moderate mechanical strength, a second layer of highly permeable poly(dimethylsiloxane) (PDMS) with thickness around 4 μm was coated directly on top of the thin glassy layer, by spin casting a 12 wt% PDMS/cyclohexane solution. The PDMS solution, the catalyst (OL) and crosslinking agent (V24) were kindly donated by Wacker Silicons Co. According to the series resistance model [40], the permeability of composite membranes is given by the following equation,

$$\frac{l_{\text{composite}}}{P_{\text{composite}}} = \frac{l_{\text{PDMS}}}{P_{\text{PDMS}}} + \frac{l_{\text{Matrimid}}}{P_{\text{Matrimid}}} \quad (1)$$

where l is the thickness and P is the permeability. The effect of the PDMS layer is essentially negligible because it only contributes 4% or less to the overall permeability, and it does not undergo

physical aging itself or appear to affect the physical aging behavior of the glassy layer over time [41].

The wafers with the bilayer films were transferred onto a hot plate and annealed at 110 °C for 15 min to crosslink the PDMS and remove any residual solvent. The bi-layer films were then lifted from the wafer by using thin wire frames with assistance of deionized water, followed by drying in an oven at 105 °C for 2 h.

Since physical aging of glassy polymers strongly depends on the prior thermal history, both thick and thin Matrimid films were annealed at 325 °C ($T_g = 310$ °C) for 15 min in a N₂ atmosphere and then rapidly quenched to room temperature. By using this protocol, all the films had a well-defined thermal history prior to all the experiments in this study. The time at which a film was quenched was recorded as the time zero for aging purposes.

The films were then masked by two pieces of aluminum tapes with a small piece of Anopore™ ceramic disc as a support. The prepared samples with their time zero marks were stored in a chamber at ambient pressure and 35 °C until permeation measurements were made.

2.2. Gas permeation

Both single and mixed gases permeation experiments were performed using homemade constant volume permeation cells. The downstream volumes were designed to be very small (~50 ml) in order to accumulate gas mixtures with enough pressure in a short period (2–10 min) for quantification of the amount and concentration of permeate. The permeate was analyzed by an Agilent 7890A gas chromatography system equipped with one PLOT-Q and one molecular sieve 5A column. The detailed description of this setup can be found elsewhere [42]. All gases were obtained from Soxal, Singapore.

When working with gas mixtures, especially those containing CO₂ at elevated pressure, it is useful to express the permeation driving force in terms of a fugacity rather than a partial pressure difference, due to the non-ideal behavior of the gases. In this study, the fugacity coefficients of CO₂, N₂ and CH₄ were calculated with the software ThermoSolver using the Peng and Robinson equation of state (EoS) [43]. To obtain the permeability of individual gases, the fugacity difference between the upstream and downstream was employed instead of the pressure difference. The downstream fugacity (up to 0.14 atm) can be ignored compared to the upstream fugacity (2–48 atm) in the constant volume method, so the upstream fugacity was used directly in the equations.

The pure gas permeability was calculated from the steady state rate of pressure accumulation in the downstream volume (dp/dt) according to the following equation:

$$P = \frac{VL}{ATf} \left(\frac{dp}{dt} \right) \quad (2)$$

where P is the membrane gas permeability given here in Barrer (1 Barrer = 1×10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹), V represents the volume of the downstream volume, A is the effective membrane area, L refers to the membrane thickness, T is the operating temperature (K) and f indicates the upstream fugacity.

Mixed gas permeation tests were performed at 35 °C in the range of 2–48 atm, and two binary mixtures (CO₂/N₂ and CO₂/CH₄) with different CO₂/inert gas molar ratios were used as feeds. The permeability of each gas was determined according to the following equation:

$$P_i = \frac{y_i VL}{ATf_i} \left(\frac{dp}{dt} \right) \quad (3)$$

where P_i is the permeability of gas i , f_i is the upstream feed gas

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