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Physical aging of ester-cross-linked hollow fiber membranes for natural gas separations and mitigation thereof

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ABSTRACT

Like other glassy polymers, ester-cross-linked polyimide hollow fiber membranes can experience physical aging, which leads to some loss of permeation productivity. Highly quenched asymmetric structures are especially susceptible to such aging. To explore approaches to control physical aging, CO_2 conditioning and continuous CO_2/CH_4 feed tests were studied in this work. A 100 psig CO_2 conditioning overnight did not affect the aging of cross-linked hollow fibers significantly. However, periodical 15 psig CO_2 conditioning reduced the CO_2 permeance loss of cross-linked hollow fiber membranes by ~50%, compared to unconditioned ones during a 2300 h aging test. To further suppress physical aging, continuous exposure to CO_2/CH_4 feed typical of realistic continuous operations was used for hollow fiber samples. This protocol, in fact, reflects the realistic situation for use of asymmetric membranes that typically run under protracted steady state conditions. A 200 psia continuous 50/50 CO_2/CH_4 feed resulted in a CO_2 permeance loss of only up to 3%, compared the 25% loss for samples without continuous mixed gas feed during a 400 h aging test. These results suggest that physical aging may be essentially quenched as long as the membrane remains contacted with a high CO_2 partial pressure feed typical of actual aggressive feeds for which the membrane would be used. By inhibiting physical aging, periodic CO_2 conditioning and continuous CO_2/CH_4 feed provide high performance of cross-linked hollow fiber membranes for natural gas separations.

1. Introduction

Polyimides based on 4,4′-(hexafluoroisopropylidene) diphthalic anhydride in cross-linkable forms have been shown to be an attractive membrane material family for natural gas separations, with both high CO_2 permeate flux and CO_2/CH_4 selectivity [1–5]. The cross-linked hollow fibers suppress CO_2 induced plasticization, thereby maintaining CO_2/CH_4 selectivity in aggressive feeds [5]. This family also shows high separation performance in the presence of high-level hydrocarbon impurities, such as toluene, heptane and related contaminants sometimes present in natural gas [6–8]. Despite the intrinsically excellent separation properties, ester-cross-linked polyimide hollow fiber membranes can show physical aging, resulting in a loss of CO_2 permeance in some cases [8,9]. This study aims to better understand the aging phenomenon and to identify approaches for its mitigation.

Physical aging is a common characteristic of glassy polymer membranes with unrelaxed free volume resulting from rapid quenching from the rubbery state or casting from solutions [10]. Due to the "non-equilibrium" nature of glassy polymers [11], such materials tend to relax towards "equilibrium" states, resulting in changes of physical properties, including transport properties [12,13]. It is believed that loss of fractional free volume (*FFV*) causes a drop of permeability of membranes [14]. Since physical aging also causes a loss of productivity [15–17], it is useful to seek methods to moderate this process, thereby maintaining the intrinsically high performance of membranes.

To affect physical aging rates of glassy polyimides, attempts have been made by using CO_2 conditioning, i.e., by exposing samples to this highly soluble penetrant to increase gas permeate fluxes and excess free volume of the polymer [18–21]. Kim et al. studied both physical aging and CO_2 conditioning of cross-linked dense film membranes [18]. They showed that 2 atm CO_2 conditioned cross-linked *dense film* membranes experienced similar physical aging rates as unconditioned ones during a 2000 h experiment. Nevertheless, physical aging of *hollow fibers* can behave differently from *dense films* due to the large amount of free volume trapped in hollow fibers during the rapid quenching spinning process, compared with the slow evaporation of solvents to prepare dense film samples [9]. Furthermore, the asymmetric morphology of *hollow fiber* membranes can show significantly different permeability increases following CO_2 conditioning, as compared to the symmetric *dense film* membranes [22,23]. Therefore, this work reports effects of

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CO_2 conditioning on physical aging of cross-linked hollow fibers, which is the industrially preferred configuration of membranes, due to high surface-to-volume ratio. Moreover, continuous CO_2/CH_4 feeds were also applied to the hollow fibers to suppress physical aging and thereby achieve high separation productivity for extended time natural gas separations.

2. Background and theory

2.1. Gas transport in membranes

For gas separation polymeric membranes, the so-called sorption-diffusion model describes transport of gases. In this model, gas molecules first sorb in the upstream of a membrane and then diffuse through the membrane due to the partial pressure or fugacity difference across the membrane. A gas mixture can be separated by the membrane, because gas molecules have different solubilities and diffusivities in the membrane. The separation productivity of a dense film membrane is characterized by the permeability, P, of a specific gas, which is the production of diffusivity, D, and solubility, S, as shown in Eq. (1):

$$P = D \cdot S \tag{1}$$

The permeability of penetrant i, P_i, is defined by the flux of penetrant i, n_i, normalized by the membrane thickness, l, and the partial pressure or fugacity difference, Δp_i, across the membrane, viz., [11]:

$$P_i = \frac{n_i \cdot l}{\Delta p_i} \tag{2}$$

The common unit of permeability is the Barrer where,

$$1\text{Barrer} = 10^{-10}\left(\frac{\text{cc(STP)}\cdot\text{cm}}{\text{cm}^2\cdot\text{s}\cdot\text{cmHg}}\right) \tag{3}$$

For asymmetric hollow fiber membranes, the separation productivity is characterized by the permeance, P_i/l, which is the pressure or fugacity difference normalized flux of permeant i, through Eq. (4).

$$\frac{P_i}{l} = \frac{n_i}{\Delta p_i} \tag{4}$$

In Eq. (4), P_i is the permeability; l is the effective selective skin layer thickness; Δp_i is the pressure (or fugacity) difference. Under aggressive high pressure feed conditions, the above transmembrane partial pressure differences must be replaced by the transmembrane fugacity difference to reflect the material property of the membrane.

The common unit of permeance is the GPU, defined in Eq. (5):

$$1\text{GPU} = 10^{-6}\left(\frac{\text{cc(STP)}}{\text{cm}^2\cdot\text{s}\cdot\text{cmHg}}\right) \tag{5}$$

On the other hand, the selectivity, α_{ij}, is commonly used to characterize the separation efficacy of a membrane, represented by the ratio of permeability or permeance of penetrant i to penetrant j, via Eq. (6):

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{P_i/l}{P_j/l} \tag{6}$$

2.2. Physical aging

As discussed in Section 1, glassy polymers exist in “non-equilibrium” states by virtue of molecular scale unrelaxed free volume trapped during rapid quenching from the rubbery state or casting from solutions [10]. The unrelaxed volume is represented as V_g-V_l, where V_g is the actual glassy volume and V_l is the volume of the densified glass, as shown in Fig. 1.

The unrelaxed volume in glasses and fractional free volume, *FFV*, are related; however, in a complex way. Nevertheless, changes in the unrelaxed volume also affect *FFV*, and Park and Paul correlated the permeability of a polymeric membrane with the *FFV* using Eq. (7) [24].

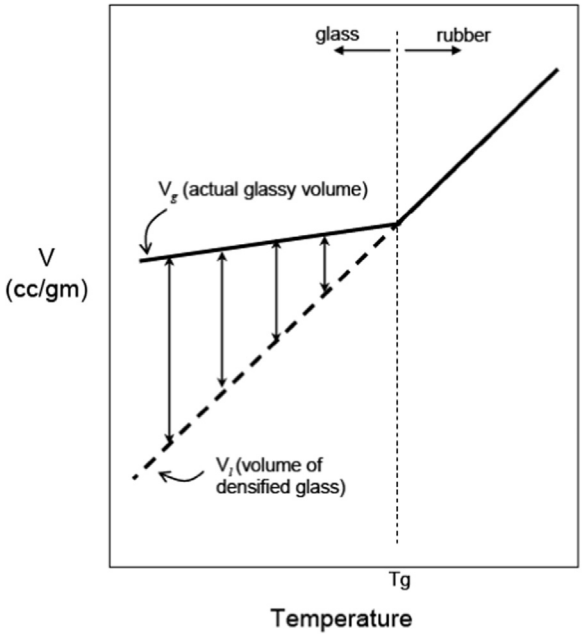

Fig. 1. Schematic showing hypothetical “unrelaxed free volume (V_g-V_l)” in a glassy polymer as a function of temperature [10].

$$P = A\exp\left(\frac{-B}{FFV}\right) \tag{7}$$

where A and B are constants for a particular gas.

Previous research has shown that physical aging leads to a loss of permeability for dense film membranes [14]. Since A and B in Eq. (7) are penetrant-dependent constants, the decrease of permeability indicates a loss of *FFV* of polymers during physical aging. The loss of permeability is due to both polymer lattice contraction and the diffusion of unrelaxed free volume, as illustrated schematically in Fig. 2 [14,16,25,26].

The lattice contraction process is pervasive throughout the whole membrane and independent of the sample size [26]. On the other hand, for simplicity, assuming the diffusion of free volume follows an effective Fick's second law type of diffusion, the free volume flux will be inversely proportional to the square of the membrane thickness for a given aging time [14]. Therefore, it is believed that thinner dense film membranes tend to age faster than thicker ones. To check this assumption, researchers have studied different dense film thicknesses

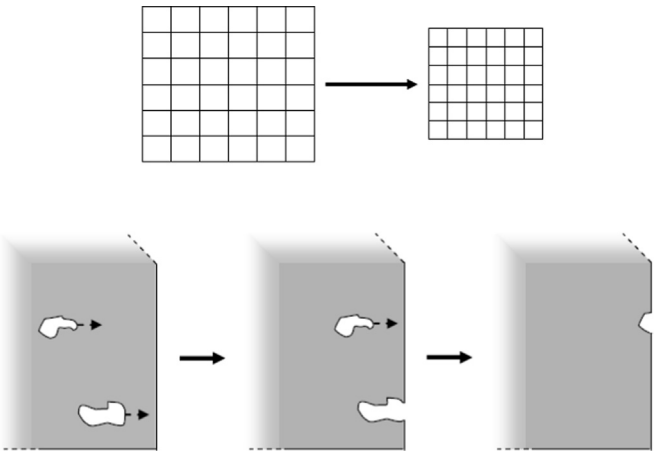

Fig. 2. Physical aging mechanisms in polymeric membranes: lattice contraction (top) and diffusion of free volume (bottom) [14].