



## Physical aging of polyetherimide membranes



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### ARTICLE INFO

#### Article history:

Received 27 June 2015

Received in revised form

1 September 2015

Accepted 3 September 2015

Available online 8 September 2015

#### Keywords:

Physical aging

CO<sub>2</sub> removal

Heat treatment

Membrane storage

Physical-aging model

### ABSTRACT

This paper presents a study of the physical aging of asymmetric polyetherimide (PEI) flat membranes. The effects of storage type (under vacuum, atmospheric air, and pure argon), the presence of polydimethylsiloxane (PDMS) coating, membrane heat-treatment temperature, and membrane-preparation PEI wt% on the physical aging were investigated over 240 days by monitoring CO<sub>2</sub> permeance and CO<sub>2</sub>/CH<sub>4</sub> selectivity of the membranes. The feed was a 10/90 V/V CO<sub>2</sub>/CH<sub>4</sub> binary gas mixture. Physical aging was quantified in terms of CO<sub>2</sub> permeance ultimate change and aging time constant, as well as CO<sub>2</sub>/CH<sub>4</sub> selectivity ultimate change and aging time constant. New first-order physical-aging models were proposed and shown to predict the physical aging accurately. This study indicates that physical aging decreases the permeance but increases the selectivity. The membranes age less when (a) they have a PDMS coating, (b) they are prepared with a higher PEI wt%, and (c) they have a higher annealing temperature, especially above the glass transition temperature. Membranes stored under vacuum age at a slower rate than those stored under atmospheric air or pure argon.

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## 1. Introduction

The removal of CO<sub>2</sub> (an acid gas) from natural gas is of great importance in the chemical and petrochemical industries (Kim and Lee, 2014; Chua et al., 2013; Ma and Koros, 2013a; Sanders et al., 2013a; Vaughn and Koros, 2014). Compared to conventional methods of separating CO<sub>2</sub> from other gases, such as absorption, adsorption and cryogenics distillation, membrane separation requires less energy, is of lower cost for smaller units (Hinchliffe and Porte, 2000; Basafa and Pourafshari Chenar, 2014), offers ease of scale-up and simple operation, and allows for a compact, portable and environmentally-friendly technology (Baker and Low, 2014; Shao et al., 2009; Madaeni et al., 2011; Qiu et al., 2013; Kraftschik and Koros, 2013; Ma and Koros, 2013b). Among different materials, polymers have been used widely for the membrane fabrication (Koros, 2004; Sanders et al., 2014; Lin, 2014; Lin and Freeman, 2005). However, the trade-off between permeability and selectivity is a disadvantage of polymer membranes, as indicated by Robeson's upper bound curve (Robeson, 2008; Lin and Yavari, 2015).

Polyetherimide (PEI) is used as a membrane material because of its good chemical and thermal stability as well as its acceptable permeability and selectivity (Wang et al., 1998; Barbari et al., 1989). Peinemann (1987) reported CO<sub>2</sub>/CH<sub>4</sub> selectivity of 30–40 and 114–168 in the case of He/N<sub>2</sub> for flat-sheet asymmetric PEI membranes. Kneifel and Peinemann (1992) prepared porous and dense PEI hollow fiber membranes fabricated using an N-methyl-2-pyrrolidone/7-butyro-lactone solvent system; they reported a selectivity of about 170 for He/N<sub>2</sub> separation. Wang et al. (1998) fabricated PEI hollow fiber membranes for separation of N<sub>2</sub> from N<sub>2</sub>/He, N<sub>2</sub>/H<sub>2</sub>, N<sub>2</sub>/CO<sub>2</sub>, N<sub>2</sub>/CH<sub>4</sub>, and N<sub>2</sub>/Ar mixtures. Ren and Deng (2010) created polyetherimide membranes using an N-methyl-2-pyrrolidone (NMP)/non-solvent system and investigated the effects of various non-solvents on membrane morphology. Peng et al. (2010) fabricated hollow fiber PEI membranes in NMP and dichloromethane with an ultra-thin dense-selective layer for O<sub>2</sub>/N<sub>2</sub> separation and reported a selectivity of about 2–7.5. Simons et al. (2010) investigated CO<sub>2</sub> sorption and transport behavior of PEI and obtained a selectivity of about 40–60 for CO<sub>2</sub>/CH<sub>4</sub> separation. Naim and Ismail (2013) investigated the performance of PEI membranes in CO<sub>2</sub> removal. Arabi Shamsabadi et al. (2014) studied the use of PDMS/PEI membranes for H<sub>2</sub>/CH<sub>4</sub> separation.

Because of their high thermal, chemical and mechanical

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stabilities, low plasticization, and controllable pore size, inorganic materials have been used widely as membranes (Ismail et al., 2015). Metal, metal oxide, carbon, and zeolite type membranes (Venna and Carreon, 2015; Darmavan et al., 2015; Koros et al., 2014; Clarizia et al., 2008) have been used as membrane materials for gas separation.

PDMS coated membranes have been used widely in heavy hydrocarbons separation (Scholes et al., 2010; Fang et al., 2015). The PDMS coating layer fills defects of membranes fabricated by the phase inversion method. PDMS has appealing structural properties such as unique flexibility of the siloxane backbone, low intermolecular forces between the methyl groups, and high bonding energy of the siloxane bond (Madaeni et al., 2012). Studies have been carried out to investigate the effects of coating conditions, such as the concentration of coating solution, solvent type, coating temperature, and number of coating layers, on the membrane performance (Liu, 2008; Shieh and Chung, 2000; Peng et al., 2003).

Physical aging is the phenomenon of membrane performance degradation while the membrane is stored (not in use). It affects the free volume of glassy polymers especially far below of their glass transition temperatures (Huang and Paul, 2004; Pfromm and Koros, 1995; McCaig and Paul, 2000; McCaig et al., 2000) and is caused by changes in the macroscopic properties of glassy polymeric membranes, which depend on molecular properties of the membranes (Fu et al., 2008a). Glassy polymers are non-equilibrium materials, because of their excess free volume and the kinetic constraints on their segmental motion that prevent them from reaching their equilibrium properties completely when they are below their glass transition temperatures. However, even in their kinetically constrained glassy state, polymers undergo local segmental motions, which result in a steady enhancement in the density of polymers, and in turn in a reduction in their free volume to the thermodynamic equilibrium value (Struik, 1978). Physical aging slows down over time, because the excess free volume, which is the driving force for the aging, declines gradually. Furthermore, as the free volume decreases, the chain mobility declines, leading to less segmental movements that help reorganize the polymer chains. Physical aging has been shown to lower gas permeability of polymers and change their specific volume, enthalpy and entropy (Sanders et al., 2013b). In the physical aging, the permeability of each component of the gas stream decreases with time. However, because of a higher decline in the permeability of the less permeable component (i.e., CH<sub>4</sub>) with time, the selectivity, which is the ratio of the permeabilities of the two components, increases with time. In view of these, the permeability change of the more permeable component is a more decisive measure of the degree of aging.

In this study, PDMS/PEI composite membranes are prepared by the phase inversion method and effective coating (Kargari et al., 2014). To study the physical aging (performance degradation) of the membranes, the CO<sub>2</sub> permeance and selectivity of the membranes are investigated experimentally. Effects of the coating layer, membrane-preparation PEI wt%, heat-treatment temperature, and storage type on membrane physical aging are investigated. New first-order empirical models are proposed to predict the membrane performance-degradation with time.

## 2. Experimental

### 2.1. Materials

PEI was obtained from Sigma–Aldrich (USA) in pellet form, and iso-propanol, *n*-hexane, and anhydrous 1-methyl-2-pyrrolidinone (EMPLURA<sup>®</sup>, 99.5%, water<0.1%) from Merck (Germany). Demineralized water was from Marun Petrochemical Company, Ahwaz,

Iran. PDMS and curing catalyst received from ZH-mark (Italy). All chemicals were used as received. Pure gases including CH<sub>4</sub> (99.9%) and CO<sub>2</sub> (99.9%) were supplied by Technical Gas Services (Dubai, UAE).

### 2.2. Membrane preparation and performance evaluation

The phase-inversion method was used to prepare asymmetric PDMS/PEI composite membranes. After degassing the polymer solution, uniform films were casted with 300 μm thickness on a glass plate by a film applicator. The casted film along with the glass plate was smoothly immersed in a water–isopropanol (4:1) bath to accomplish the phase inversion, where exchange between the solvent and the non-solvent was induced. Then the membrane was immersed in demineralized water for 24 h. Finally, the membranes were placed between two sheets of filter paper and dried for 24 h at room temperature. Concentrations above the polymer-solution critical concentration reported in Arabi Shamsabadi et al. (2013a) and Arabi Shamsabadi et al. (2013b) were used, and sequential dip-coating with different PDMS concentrations (3, 5, 10, and 15 wt. %) was applied to obtain an effective PDMS coating thickness of 9 μm. To investigate the effects of membrane-preparation PEI wt%, PDMS coating, heat treatment temperature, and storage type on the membrane physical aging, the following membranes were fabricated:

- Set 1: Membranes with a heat treatment temperature of 35 °C, 28 wt% PEI, and:
  - PDMS coating: 18 membranes
  - No PDMS coating: 18 membranes
- Set 2: Membranes with a heat treatment temperature of 35 °C, PDMS coating, and:
  - 25 wt% PEI: 18 membranes
  - 28 wt% PEI: 18 membranes
  - 30 wt% PEI: 18 membranes
- Set 3: Membranes with 28 wt% PEI, PDMS coating, and:
  - Heat treatment temperature of 35 °C: 18 membranes
  - Heat treatment temperature of 110 °C: 18 membranes
  - Heat treatment temperature of 220 °C: 18 membranes
- Set 4: Membranes with 28 wt% PEI, PDMS coating, and a heat treatment temperature of 35 °C: 54 membranes

To investigate the effect of heat treatment temperatures of 110 °C and 220 °C, membranes were heated at 110 °C and 220 °C (14 °C above the glass transition temperature) under nitrogen purge for 100 h followed by quenching and storing at 35 °C. The film casting of the membranes was performed during two consecutive days.

For the evaluation of the effects of PDMS coating, PEI wt%, and the heat treatment temperature on the performance degradation (aging) of the membranes, all membranes of Sets 1, 2, and 3 were stored under atmospheric air (1.020 bar pressure, 40–65% relative humidity) at 25 °C. Over a period of 240 days, on each of the days 0, 11, 20, 32, 42, 59, 118, 183, and 240, two membranes from each set were taken out of the storage room and then tested for permeance and selectivity after 1 h of gas separation to ensure steady state conditions, yielding two measurements of permeance and two measurements of selectivity. Furthermore, to prevent concentration polarization in the upstream of the membranes, the retentate flow rate was set to be at least 100 times greater than the permeate flow rate (Vaughn and Koros, 2014). The tested membranes were then discarded.

For the evaluation of the effect of the storage type on the performance degradation (physical aging) of the membranes, first 18 membranes from Set 4 were stored under atmospheric air at 25 °C

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