Gas transport properties of interfacially polymerized polyamide composite membranes under different pre-treatments and temperatures

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ABSTRACT

Thin-film composite reverse osmosis membranes were dried under different membrane pre-treatment procedures and evaluated at increased temperatures by gas separation tests. The obtained permeance and selectivity values indicated the presence of highly-permeable regions in the dry samples of the commercial membranes.

Treatment with ethanol–hexane in a solvent exchange process, as well as membrane immersion in *t*-butanol followed by freeze drying, increased the gas permeance by a factor of 1.8 to 9, and from 1.6 to 3.2, respectively, by comparison with room temperature and oven drying. Nevertheless, a Knudsen-diffusion transport mechanism was dominant after both pre-treatments.

The permeation temperature remarkably influenced gas selectivity and permeance, and a maximum He/N$_2$ selectivity occurred at 150 °C with considerable high permeance results, which may suggest the use of polyamide membranes as alternative materials for high-temperature separation processes. The temperature-induced changes in the polymer structure and in the transport of compounds can be explained by Knudsen and activated diffusion mechanisms throughout a highly-permeable regions and a dense polyamide matrix, respectively.

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1. Introduction

The reverse osmosis (RO) process, which uses polymeric semipermeable membranes to achieve molecular separation, is now an economic and universally accepted technique, with the major breakthrough in this field being achieved with the development of thin-film composites membranes (TFC) [1]. These TFC materials generally consist of three layers: a polyamide barrier skin, a porous support layer (often polysulfone), and a non-woven polyester. Both the polysulfone and polyester layers provide mechanical support for the polyamide layer, which generally provides selectivity to the membrane. The thin selective upper layer and porous support can be separately optimized to give high permeability and selectivity.

Today, most commercial RO TFC membranes are formed *in-situ* by the interfacial polymerization of an aromatic polyamine such as *m*-phenylenediamine (MPD) with one or more aromatic polyacyl halides (for example, trimesoyl chloride (TMC)). These aromatic-based membranes exhibit good performance in many desalination and water purification applications and are already in mass production [2,3] because of the high flux and high rejection provided by the thin separating layer in the composite structure. Aromatic polyamide materials, however, have not merited comparatively special attention for gas separation either in dense membranes [4–6] or composite structures [6–12] despite the mechanical and chemical properties that make them attractive for this separation process [13].

Since the active layer is extremely thin in TFC membranes, treatment prior to their use for gas separation is a very sensitive process. Usually this pre-treatment involves two general steps: (1) cleaning of the membrane surface by a solvent, and (2) drying of the residual solvent from within the membrane structure. The water-swollen hydrogel that fills the pores in the support membrane becomes a rigid glass when dried for use in gas separation, giving very low gas permeability, although relatively high selectivities may yet be achieved [2]. Therefore, membrane pre-treatment can cause shrinkage and swelling, but can also cause the removal of residual monomers or additives and morphological changes that effectively varied membrane properties [7,8,14–21].

Additionally, RO membranes are generally perceived to have a non-porous separating layer where transport occurs via a solution–diffusion process, but an examination of the literature indicated that some dry RO membranes exhibits highly-permeable regions that are usually attributed to the presence of membrane defects [7,8,16–19]

formed either during the membrane preparation or during drying treatments. For instance, Louie et al. [7] identified defects in commercial polyamide RO membranes that were eliminated when the membrane surface was coated with a polyether–polyamide block copolymer, suggesting that using n-butanol as a solvent for applying coatings negatively affects water and gas permeation. Kuehne et al. [19] studied the effect of varying processing conditions during TFC RO membrane fabrication and reported an enhanced flux after washing the membrane with glycerol and organic salts. They attributed rejection differences between membrane samples to membrane imperfections. Jezowska et al. tested RO polyamide membranes after a cleaning step concluding that membrane homogeneities could be partially caused by improper pre-treatment of the membrane material [16]. However, Sridhar et al. [11] tested interfacial polymerized TFC membranes with an ultrathin defect-free polyamide skin layer for gas separation. The limited selectivities obtained, in comparison to that of a dense film, suggested consideration of the presence of less cross-linked regions in the polyamide separation layer. Li et al. [12] recently compared defect and defect-free interfacially-polymerized TFC membranes, attributing the deterioration of gas selectivity not only to membrane defects, but to cross-linked polyamide layer density. As a consequence, a clear understanding of the TFC RO polyamide membrane pore structure has not yet been achieved.

In general, the transport of molecules at different temperatures is dependent upon the available free volume in the polymer matrix, as well as sufficient energy of the molecules to overcome attractive forces between chains. In this sense, analysis of the change in membrane permeation due to polymer flexibility with temperature is useful for characterization of the TFC RO polyamide membrane pore structure. Because RO membrane pores are equal to, or only a few times the size of gas molecules, transport across these membranes can be expected to occur in the intermediate regions from Knudsen diffusion and activated diffusion. Ideally, this mechanism enables gas molecules to be separated, while the separation of those gas molecules is difficult if their diameter sizes are similar [22].

Since different conditions can influence membrane heterogeneity and the transport of compounds through the selective polyamide layer, the main objective of this work was to systematically explore whether drying pre-treatments and temperature can result in improvements in asymmetric RO membranes for gas separation. To the best of our knowledge, no studies of the effect of increasing permeation temperature on the separation performance of TFC RO polyamide membranes have been reported. The effects are discussed in terms of permeance and separation factor variations. An additional part of this work was devoted to determining whether such effects also produce the transformation of inhomogeneous regions into denser structures, thus defining the transport mechanism through the membrane.

A clearer understanding of the effects of these processes on membrane properties will aid in the development of improved membranes with better separation performance for high-temperature processes.

2. Experimental

2.1. Materials

Three commercial RO membranes were provided by Niito Denko (Japan) and applied in this study: SWC5 (seawater membrane), ESPA2 (energy-saving RO membrane), and CPA5 (high-rejection RO membrane). Membrane samples were vacuum sealed in a polyethylene bag containing less than 1% sodium

Table 1
Water permeability and salt rejection of RO membranes as listed by the provider.

Membrane	Test conditions	Water permeability [L/(m^2 h bar)]	Salt rejection [%]
SWC5	32,000 ppm; 5.5 MPa; 25 °C	1.38	99.8
ESPA2	1500 ppm; 1.05 MPa; 25 °C	4.15	99.6
CPA5	1500 ppm; 1.55 MPa; 25 °C	3.28	99.7

meta-bisulfite solution. Table 1 shows the water permeability and salt rejection in the RO membranes under the conditions listed in the provider information data sheet.

The membranes consisted of a thin-film-composite with a top-skin aromatic polyamide, PA, layer (~200 nm), a middle microporous polysulfone, PSF (~40 μm), and a bottom polyethylene terephthalate, PET, layer (~120 μm). The specific chemical composition of the PA layer is proprietary information of the supplier.

PA membranes were additionally formed in-situ by interfacial polymerization [23] and applied in some sections of this work for comparison. Briefly, 1 ml of aqueous solution of 1,3-phenylenediamine (m-phenylenediamine, MPD) (2 wt%) and sodium lauryl sulfate (0.15 wt%) was poured on a PSF membrane, and then the excess of the solution was removed softly with filter paper. Subsequently, a 1 ml hexane solution of 1,3,5-benzenetricarbonyl trichloride (trimesoyl chloride, TMC) (0.1 wt%) was poured on the support. After a 1-min polymerization reaction, the excess solution was drained, and the membrane was dried in air for 15 min. Finally, the membrane was rinsed with deionized water.

All high purity chemicals of analytical grade applied in this study were provided by Sigma Aldrich (Japan).

2.2. Membrane pre-treatment methods

Based on a review of the available literature, three different common membrane pre-treatments were selected [11,24,25]. The procedures were adapted and applied to membrane samples prior to their use in gas separation:

- *Room Temperature–Oven* (*RTO*): Membranes were washed several times in a pure-water bath, then dried at room temperature for 24 h, and finally placed in an oven at 120 °C for 30 min [11].
- *Ethanol–Hexane* (*EH*): Membranes were washed several times in a pure-water bath, then immersed in ethanol for 5 min and afterwards soaked in a hexane bath for 1 min. Finally, the solvent was evaporated at room temperature for 15 min [11,24].
- *Freeze Drying* (*FD*): Membranes were washed several times in a pure-water bath, then immersed in 50, 75, 90, 95, and 100 wt% t-butanol aqueous solutions for 15 min. Then, membrane samples were placed in pure t-butanol in freeze-dried equipment under vacuum for 2 h [25].

2.3. Gas separation experiments

Membrane samples (2.21 cm^2) were tested in a stainless permeation cell using He, H$_2$, CO$_2$, O$_2$, N$_2$, C$_3$H$_8$, and SF$_6$ at temperatures that ranged from ambient (room temperature, 16 ± 3 °C) to 200 °C in an oven. A schematic drawing of the experimental apparatus appears in Fig. 1. The feed gas pressure was set at 2.5 bar, and the permeate was at atmospheric pressure. The flow rate of the permeating gas was measured using a bubble flow meter. Prior to testing, membranes were under vacuum with a He flow for 1 h. Additionally, samples were under vacuum for