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Thermally rearranged mixed matrix membranes for CO_2 separation: An aging study

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ABSTRACT

In this work, the aging behavior of a thermally rearranged polybenzoxazole-co-imide (TR-PBOI) mixed matrix membrane loaded with 0.5 wt.% of oxidized multi-wall carbon nanotubes (MWCNT) was evaluated and then compared to a pure TR polymeric membrane prepared from the same precursor. To the best of authors knowledge, this is the first report of a mixed matrix membrane being prepared through the dispersion of MWCNTs within a thermally rearranged polymer matrix for CO_2 separation. Microporous structures were created in both membranes when thermally rearranged at 375 °C, facilitating fast mass transfer ideal for membrane gas separation. The TR mixed matrix membrane with oxidized CNTs demonstrated improved separation properties with regard to both permeability and selectivity compared to the pure TR polymeric membrane due to a greater degree of thermal rearrangement (11.3%) than what was exhibited by the TR membrane (6.7%). Moreover, the high CO_2 solubility typical of TR polymers coupled with diffusivity enhancements improved the CO_2/N_2 selectivity. The addition of oxidized CNTs to the TR-PBOI polymer did not significantly influence the aging behavior of the mixed matrix membrane. Both pure TR-PBOI and mixed matrix membranes exhibited an increase in CO_2 selectivity due to physical aging. The improved separation properties in conjunction with an unchanged membrane stability over time suggested that the addition of CNTs to pure TR membranes could be an excellent approach toward improving the performance of thermally rearranged membranes applied toward gas separation.

1. Introduction

Today membrane technology for gas separation (GS) is a well-consolidated technique, in various cases competing with traditional operations. The separation of H_2 from refinery industrial gases, natural gas dehumidification, separation and recovery of CO_2 from biogas and natural gas are some examples in which membrane technology is successfully used in industry. For various years, membrane operations have been used for the separation of air components or oxygen enriched air for use in several fields, including chemical and related industries, the mechanical field, food packing and so forth. Currently, membranes dominate the fraction of the nitrogen market for uses with a productive capacity of less than 50 ton/day and relatively low purity (nitrogen 95–99.5% molar).

One of the separations that more than other attracts the attention on the use of membranes is CO_2 capture for reducing greenhouse emissions. Power and hydrogen production, heating systems (for example, in the steel and cement industries) and natural gas and biogas purification, are examples of circumstances in which carbon dioxide is produced in huge (thousands of ton/h) streams. Although carbon dioxide separation from hydrogen and methane streams has long been used since the high value of these streams (Basu et al., 2010; Scholes et al., 2012), recent constraints and regulations on CO_2 emissions from power plants have forced researchers to focus on the separation of CO_2 from flue gas streams (Brunetti et al., 2010; Li et al., 2013a; Daal et al., 2013).

In the last few decades, the development of polymeric membranes with high free volume distributions, such as polymers with intrinsic microporosity (PIMs), thermally rearranged (TR) polymers, and Tröger's base polymers, have been actively researched, especially as they relate to gas separation (Brunetti et al., 2014), where these membrane are considered to be ideal candidates for low-energy gas separation applications like flue gas treatment due to their high permeability and good selectivity.

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Nomenclature

List of symbols

A	Area, m^2
Mw	Molecular weight, $g\,mol^{-1}$
P	Pressure, bar
Pe	Permeability, Barrer
Q	Feed flow rate, $m^3\,s^{-1}$

Superscipts

Feed	Feed phase referred to
Membrane	Membrane referred to
Permeate	Permeate phase referred to
Retentate	Retentate phase referred to

Greek letters

α	Membrane selectivity, –
δ	Separating layer thickness, m

In particular, it has already been proved as TR polymer membranes are among the most scalable microporous polymer membranes, thanks to their outstanding mechanical, thermal and chemical resistance coupled with the easy handling and processability. The possibility of using these highly permeable hollow fibre membranes in carbon capture and sequestration (CCS) systems means a significant reduction of the membrane area required for treating a set of feed stream with respect to other "conventional" glassy polymer membranes, thus, in other words significantly less footprint occupied by the installation. In post-combustion capture, as well as in biogas and natural gas treatment, this figure would significantly affect the final cost of the operation, making more profitable for the use of membranes as separation technology for these huge gaseous streams.

Amid these advantages, a big challenge lying in the appropriate scaling-up from laboratory-scale hollow fiber TR membrane modules to industrial-scale modules, which requires a thorough understanding and remains the primary drawback of these high free volume polymer membranes is their rapidly declining separation performance due to physical aging, especially with regard to permeability (Hutchinson, 1995; Pfromm and Koros, 1995; Xia et al., 2014; Lau et al., 2014; Yong et al., 2015a; Cui et al., 2011). This issue is more relevant than in low free volume glassy polymers and much faster with regard to a high initial permeability. Moreover, as observed by Wang et al., (2014a,c) with other TR polymer membranes (derived from an *ortho*-functional polyimide based on 2,20-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride(6FDA) and 3,30-dihydroxy-4,40-diamino-biphenyl(HAB), 6FDA-HAB-TR) who performed a detailed study related to the age dependence of membranes with varied thicknesses, thinner membranes aged faster than thicker ones, amid consisting of the same material. Physical aging occurred in all PIMs (Swaidan et al., 2015) due to a high free volume. Analogously, the same processes occur in TR polymers (Brunetti et al., 2016), due to the presence of relatively flexible segments in their backbones, e.g. 6F groups normally found in TR, which induce polymer relaxation.

TR polymer membranes exhibit excellent separation performance due to their microporous structure, whose cavity sizes and distributions can be tuned through variations in precursor and treatment protocols (Park et al., 2007; Kim and Lee, 2015; Gleason et al., 2015; Li et al., 2013b; Han et al., 2010; Jung et al., 2010; Woo et al., 2015) targeting size-sieving effects that can promote specific separations. These microporous membranes are often proposed for CO_2 separation due to their reciprocal high affinities leading to CO_2 preferential adsorption on Langmuir sites (Cersosimo et al., 2015).

This implies, firstly, a reduction in the sorption capacity for permanent gases in the surrounding region, thus decreasing the solubility of permanent gases in the polymer (Raharjo et al., 2007a), and secondly, a hindering effect slowing the diffusion of light gases, decreasing the permeability of these gases through the polymer matrix (Raharjo et al., 2007b).

Most recently, hydroxyl polyimide-co-polyimide (HD5) precursors have been used to prepare thermally rearranged poly(benzoxazole-co-imide) (TR-PBOI) polymer membranes. The synthesis of hydroxyl copolyimides incorporating a rigid non-TR-able diamine moiety has been proved to improve the mechanical properties of the TR membranes, making easier for their applicability at industrial scale (Woo et al., 2015). These membranes are less "performant" than the other TR, indeed it is interesting to find a way to improve their properties, owing to their better scalability and easier handling. To prevent physical aging due to molecular chain collapse, a number of strategies have been proposed, such as the use of polymer blends (Gomes et al., 2005; Visser et al., 2007), thermal curing (Li et al., 2012), UV cross-linking (McCaig and Paul, 1999) and the addition of nanoparticles (Lau et al., 2014; Yong et al., 2015b; Olivieri et al., 2015a). Recently, Brunetti et al. (Brunetti et al., 2016) instead proposed an in-situ restoring procedure to recover the separation properties of aged TR polymer membrane modules.

Among the four aforementioned methods, the functionalization of the polymer matrix by the addition of rigid fillers can modify the microstructure of the membrane matrix, influencing the free volume distribution and hindering densification of the polymer matrix. Mixed matrix membranes are composite materials considered to be among the most promising candidates for gas separation, synergistically coupling the characteristics of an organic polymer with that of homogeneously dispersed inorganic fillers (Favvas et al., 2014). Compared to pure polymer membranes, many polymer-inorganic mixed matrix membranes exhibit improved separation properties with higher permeabilities without sacrificing or improving gas selectivity (Khan et al., 2012; Pinnau and He, 2001). Among the various possible fillers (fumed silica, zeolites, graphene, graphene oxide, carbon nanotubes, metal organic frameworks, etc.), carbon nanotubes were employed as inorganic fillers in the various matrices of both low and high free volume polymers, such as polyimide (PI) (Sanip et al., 2011; Aroon et al., 2010),polydimethylsiloxane (PDMS) (Kim et al., 2006), polyetherimide (Matrimid 5218) (Li et al., 2015), polyether-block-amide 1657 (PEBAX1657) (Yu et al., 2013; Wang et al., 2014b; Habibiannejad et al., 2016; Zhao et al., 2014), 4,4′-hexafluoroisopropylidene) diphthalic anhydride-Durene (6FDA-Durene) (Lin et al., 2015), poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylenediamine) (PBNPI) (Weng et al., 2009), brominated poly(2,6diphenyl-1,4-phenylene oxide) (BPPOdp) (Cong et al., 2007), PIM-1 (Khan et al., 2012) and others. The interaction between polymer matrix and nanotubes may disrupt the polymer chain packing thus enhancing gas diffusion, introducing more free volume voids between the polymer chains and nanoscale defects on the polymer/nanofillers interface (Khan et al., 2012). Therefore, as detailed in further sections, the presence of these fillers generally enhanced the permeability of gases. Indeed, the effects with regard to CO_2/N_2 selectivity could be either positive or negative. In particular, for mixed matrix membranes of PIM-1 (a polymer membrane structurally similar to the TR membranes), Khan et al. (2012) reported a positive effect with regard to the addition of CNTs in the polymer matrix, both in terms of gas permeability and CO_2/N_2 selectivity.

Effects of the filler on aging behavior in poly(1-trimethylsilyl-1-propyne) (PTMSP) strictly depended on the quantity dispersed within the polymer matrix (Olivieri et al., 2015b). In general, the mixed matrix membranes experienced reduced or slowed aging when compared to pure polymer membranes; however, for each