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Mixed matrix membranes for gas separation with special nanoporous fillers

Beatriz Zornoza[†], Patricia Gorgojo[†], Clara Casado, Carlos Téllez, Joaquín Coronas*

Department of Chemical and Environmental Engineering, Nanoscience, Institute of Aragon,
Universidad de Zaragoza, Centro Politécnico Superior, Maria de Luna, 3, 50018 Zaragoza, Spain
Tel. +34 976 762471; email: coronas@unizar.es

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ABSTRACT

Special nanoporous fillers for enhancing the gas separation performance of mixed matrix membranes (MMMs) are addressed in this work. The incorporation of small amounts of ordered mesoporous silica spheres (MSS) or exfoliated layered microporous titanosilicate UZAR-S1 (obtained from layered material JDF-L1) into a commercial polysulfone (PSF) membrane matrix was successfully carried out. The obtained results in terms of the separation of H_2/CH_4 and CO_2/N_2 mixtures were compared to those achieved with special fillers in the literature, such as mesoporous molecular sieves, lamellar zeolites and metal-organic frameworks. 8 wt.% MSS–PSF MMMs gave rise to H_2/CH_4 and CO_2/N_2 selectivities of 79.2 and 36.0 with H_2 and CO_2 permeabilities of 26.5 and 12.6 Barrer, respectively. 4 wt.% UZAR-S1-PSF MMM gave rise to H_2/CH_4 selectivity of 69.2 with H_2 permeability of 11.5 Barrer.

Keywords: Mixed matrix membrane; Zeolite; Exfoliated layered silicate; Ordered mesoporous silica; MOF; Gas separation

1. Introduction

Membranes are widely used in chemical industry and medical applications as barriers to separate different species. Depending on the driving force and the effective size of the penetrating substances, different processes such as gas separation (GS), pervaporation (PV), dialysis (D), nanofiltration (NF), reverse osmosis (RO), etc., can be established. Over the past few years GS processes with membranes have shown an important increase and their evolution will be briefly discussed. Attending their nature, membranes can be classified into organic/polymeric and inorganic membranes. Polymer membranes show some advantages over inorganic membranes; their ease of fabrication and operation and their low cost make them really attractive. However, they cannot operate at severe conditions of pH and temperature and their selectivity values are limited. Hybrid membranes formed by selective inorganic materials dispersed into polymer continuous matrix were proposed as a feasible option to improve the performance. These composites were named "mixed matrix membranes" (MMMs).

Inorganic materials such as carbon molecular sieves and zeolites have been used due to their adsorptive properties and nano-sized porosity which favors small molecules passing through. This combination is usually applied in PV and GS. First works on MMMs predominantly used elastomeric or rubbery polymers for GS with little improvement in the transport properties [1]. Later, research works started using glassy polymers and in most cases gaps between the fillers and the organic matrix were created. These macrovoids were a consequence of the rigidity of the polymer chains and/or the hydrophilicity of the inorganic filler and produced bypassing effect of gas molecules, i.e., when zeolite A was, introduced in a polyimide Matrimid® matrix [2]. Some authors used silane coupling agents to favor the interaction but this did not result in a significant enhancement

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*Corresponding author.

[†] These authors contributed equally to this work.

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of selectivity [3,4] or even obtained lower values compared to the pure polymer [5].

In this work, polysulfone Udel® mixed matrix membranes containing two different kinds of special fillers, ordered mesoporous silica spheres (MSSs) of 2–4 µm and high aspect ratio (HARs) delaminated titanosilicate UZAR-S1, were prepared and tested for H_2/CH_4 and CO_2/N_2 gas separation.

2. Experimental section

2.1. Preparation and characterization of fillers

MSSs were synthesized as described elsewhere [6,7]. High aspect ratio UZAR-S1 was obtained by exfoliation of the layered microporous titanosilicate JDF-L1. Experimental procedure has been described elsewhere [8].

2.2. Membrane preparation, characterization and performance

Polysulfone (PSF) Udel® P-3500 (kindly supplied by Solvay Advanced Polymers) was used for the MMMs preparation. For the pure polymer membrane, 0.4 g of polysulfone was dissolved in 3.6 ml of dichloromethane and stirred for 1 d leading to a viscous solution. The fabrication procedure for the mixed matrix membrane with MSSs or exfoliated UZAR-S1 (in a proportion of 90/10 wt.% solvent/inorganic fillers–polymer mixture) involved a previous dispersion stage of the filler in the solvent for 15 min in an ultrasound bath. PSF was then added and the whole mixture was magnetically stirred overnight. Subsequently, the membranes were cast on a flat surface, and then left overnight for natural evaporation of solvent at room temperature. Once dried, the films were placed for the same period of time at 1 kPa in a Memmert VO 200 vacuum oven at 120°C to remove the remaining solvent. Membranes with 4–8 wt.% loading of the inorganic filler were prepared. Thicknesses in the range of 75–100 µm were measured using a Micrometer (accuracy of ± 0.001 mm, Mitutoyo Corp.).

The cross-sectional area of the MMMs was analyzed by SEM with a JEOL JSM 6400 scanning electron microscope operating at a voltage of 20 kV. Samples were first introduced in liquid nitrogen and then broken off. Transmission electron microscopy (TEM) images of the MMMs were collected with a JEOL-2000 FXII microscope. Samples were embedded in an Epofix cold-setting embedding resin (15 parts of resin and two parts of hardener were mixed). The curing time was 8 h at room temperature and the cross-section pieces were sliced into 30–60 nm thick sections using a RMC MT-XL ultramicrotome with a Standard Ultraknife 45°, 3 mm diamond blade (Durkker). The thin slices were placed on carbon copper grids and observed at 200 kV.

A 15.2 cm^2 membrane area was cut from the film for the gas separation test. The membrane module consists of two stainless steel pieces with a cavity to locate the membrane and a macroporous disk support 316LSS with 20 µm nominal pore size (Mott Corp.) gripped inside with Viton® o-rings. A mass-flow controlled (MC-100SCCM-D, Alicat Scientific) 25/25 cm^3 (STP)/min H_2/CH_4 stream was fed to the retentate side of the membrane at 275 kPa while the permeate side of the membrane was swept with a 1 cm^3 (STP)/min mass-flow controlled stream of Ar at atmospheric pressure. For CO_2/N_2 separation, He was used as sweep gas. Gas concentrations in the outgoing streams were analyzed by an on-line gas micro-chromatograph Agilent 3000A equipped with TCD. Permeability in Barrer (1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)) results were obtained once the exit stream of the membrane was stabilized. The selectivities were calculated as the ratio of the corresponding permeabilities. All the permeation measurements were performed at 35°C controlled by a Memmert UNE 200 oven.

3. Results and discussion

3.1. Special fillers for MMMs

Even though zeolites were the first molecular sieves used as fillers and numerous attempts have been reported to incorporate zeolite particles in polymer matrices for gas separation, a main problem associated with mixed matrix membranes still endures. This concerns the formation of voids at the interface due to poor compatibility between polymer and external zeolite surface, so several studies have been reported on zeolite surface modification to improve the adhesion [9]. Special fillers with tuned-up morphologies may overcome this problem without the use of additional chemical agents [10].

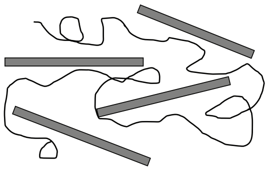
Three different kind of fillers referred here as "special fillers" have been recently used to improve this lack of interaction of both the organic and the inorganic phases: ordered mesoporous silicas (OMSs), high aspect ratio silica-based particles (HARs) and metal-organic frameworks (MOFs). The structures of the special fillers introduced here, together with some examples of MMMs, are schematically drawn in Fig. 1.

The improvement in MMMs with OMSs is due to the ordered mesoporosity of the surface which allows the polymer chain to penetrate and create a real composite at the nanometer level [7]. In fact, OMSs such as silica MCM-41 [11,12] and MCM-48 [13] have been observed to cause an increase in the permeability of pure polysulfone membranes without loss of selectivity, which suggests good contact with the polymer and benefit from the 2–3 nm pore sieving effect of the filler.

HARs obtained from exfoliation of microporous lamellar materials such as aluminophospates (AlPO) [14,15], silicate AMH-3 [16] or titanosilicate JDF-L1 [8]

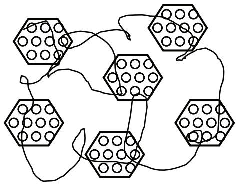
a) Exfoliated porous layered materials

Filler/polymer	(wt %)	Gas mixture
AlPO/C-PI [14]	10	CO_2/CH_4, O_2/N_2
AlPO/PPZ [15]	22	CO_2/CH_4, CO_2/N_2
AMH-3/PBI [16]	3	H_2/CO_2
UZAR-S1/PSF [8]	4	H_2/CH_4



b) Ordered mesoporous materials

Filler/polymer	(wt %)	Gas mixture
MCM-41/PSF [11]	10–30	H_2/CH_4
MCM-41/PSF [12]	40	CO_2/CH_4
MCM-41 spheres/PSF [7]	10	H_2/CH_4, CO_2/N_2
MCM-48/PSF [13]	10–20	CO_2/CH_4
MCM-48/PEI [17]	–	CO_2/N_2



c) Metal-organic frameworks

Filler/polymer	(wt %)	Gas mixture
MOF-5/PSF [18]	5	H_2/CH_4
MOF-5/PI [19]	30	CO_2/CH_4, O_2/N_2
MOF-5/PVAc [10]	15	CO_2/CH_4
$Cu_3(BTC)_2$/PDMS [20]	0–40	CO_2/N_2
$Cu_3(BTC)_2$/PSF [20]	5–10	H_2/N_2
Cu-BPY-HFS/PI [21]	10–15	CH_4/N_2, CO_2/N_2
CuTPA-PVAc [10]		CO_2/N_2
ZIF-8/PSF [22]	10	CO_2

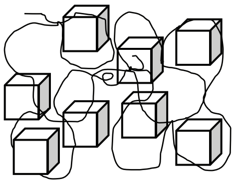


Fig. 1. Schematic layout of mixed matrix membranes prepared using the three kinds of special fillers introduced in this work: (a) exfoliated porous layered materials, (b) ordered mesoporous molecular sieves and (c) metal - organic frameworks. CPI stands for 6FDA copolyimide, PPZ for polyphospazene, PBI for polybenzimidazole, PSF for polysulfone, PEI for polyetherimide, PI for polyimide, PVAc for polyvinylacetate, and PDMS for polydimethylsiloxane.

have also been proposed as fillers in polymer membranes. Their thin morphology with high number of hydroxyl groups located on their surface makes these materials suitable for GS processes with membranes. Porous layered materials are a special kind of materials possessing an intermediate structure between clays and porous crystalline frameworks. Their modification by swelling and exfoliation gives place to microporous plate-like layers of nanoscale thickness with high area/volume aspect ratio. These thin layers that can be introduced into a polymer matrix such as glassy polyimide PBI [16], 6FDA-*co*-polyimide [14] or the rubbery polymer PPZ [15] to enhance molecular sieve properties of the resulting composite membrane material.

Very recently, some MOFs have been used to obtain MMMs with polyimide Matrimid® [19,21], PVAc [10], polysulfone and PDMS [20] for GS. MOFs are porous crystalline structures formed by metal ions or clusters and organic molecules, with yet only a few studies exploring their potential in gas transport performance [10,20]. They are very suitable to achieve a good adhesion with the polymer chains because of the affinity between the organic moieties in their framework and the polymer structure. Among MOFs, imidazolate frameworks (ZIFs) are tetrahedral networks that resemble the structure of zeolites, and the presence of these materials in a glassy polymer matrix may alter the paths in through which gases diffuse [22].

3.2. MSS- and UZAR-S1-PSF MMMs for H_2/CH_4 and CO_2/N_2 gas separation

In this section, MMMs combining OMS spheres (MSSs) with 2–4 µm diameter (see Fig. 2a) and delaminated porous titanosilicate UZAR-S1 (Fig. 2b) with polysulfone polymer matrix will be discussed according to the morphology and properties of the filler and gas separation performance achieved.

To investigate the dispersion of the MSS and UZAR-S1 particles within the polymer, the cross-sectional area of MMM samples prepared with 8 and 4 wt.% filler, respectively, were examined by SEM. As Fig. 2 shows, the filler distribution in both materials is apparently homogeneous and an optimum contact between phases was reached.

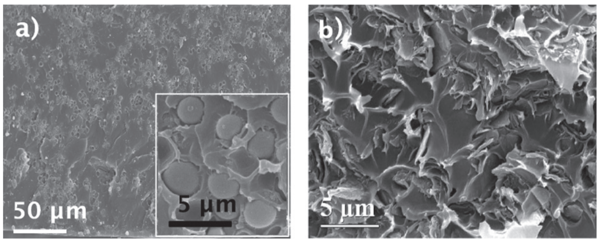


Fig. 2. SEM images of: (a) 8 wt.% MSS–PSF MMM, and (b) 4 wt.% UZAR-S1-PSF MMM.

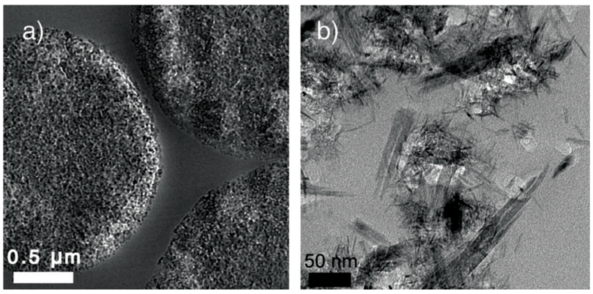


Fig. 3. TEM images of: (a) 8 wt.% MSS–PSF MMM, and (b) 4 wt.% UZAR-S1-PSF MMM.

Indeed, MSSs with MCM-41 pore structure (with 2.7 nm of pore size [7]) allows the penetration of the polymer chains (an apparent diameter of 0.9–1.2 nm was measured for a single polysulfone chain) [23] into the porosity of the material giving rise to a real composite. The nano-sized layered UZAR-S1 particles also show strong adhesion to the polymer. In consequence, gaps surrounding the particles were avoided. Fig. 3 also verify the intimate contact between both the inorganic and organic phases by TEM.

The filler loading in polymeric MMMs is often high to achieve gas separation improvements for certain gas mixtures, therefore increasing material and processing costs. In the case of polysulfone MMMs prepared with OMSs of the M41S family (loadings in the 10–40 wt.% range) the permeability increased with the loading and the best selectivity values were found at 10–20 wt.% [12–14]. A different behavior related to the gas permeability was found when adding microporous particles such as Nu(6)-2 or UZAR-S1. MMMs of these two fillers showed lower values of permeability and improvement of the selectivity [8,26]. Figs. 4 and 5 show the permeability–selectivity performance for H_2/CH_4 and CO_2/N_2 gas mixtures for the MMMs prepared with polysulfone Udel® and the fillers MSSs and UZAR-S1. Some literature results from MMMs prepared with different special fillers, same polymer and close loadings, and similar materials (including MOFs), are incorporated in the figures: 10 wt.% MCM-41–PSF MMMs [11,12], 10 wt.% MCM-48 [13], and 5 wt.% of MOFs $Cu_3(BTC)_2$–PSF MMMs [20].

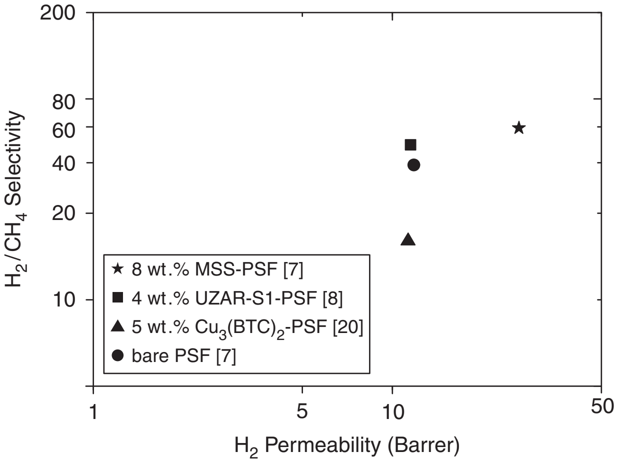


Fig. 4. H_2/CH_4 selectivity as a function of H_2 permeability at 35°C for 8 wt.% MSS–PSF MMM and 4 wt.% UZAR-S1-PSF MMM compared with results from bare PSF and other authors. Note that the pure polysulfone values for H_2 permeability and H_2/CH_4 selectivity are 9.5 Barrer and 28, respectively, in the work where $Cu_3(BTC)_2$-PSF membrane was studied [20].

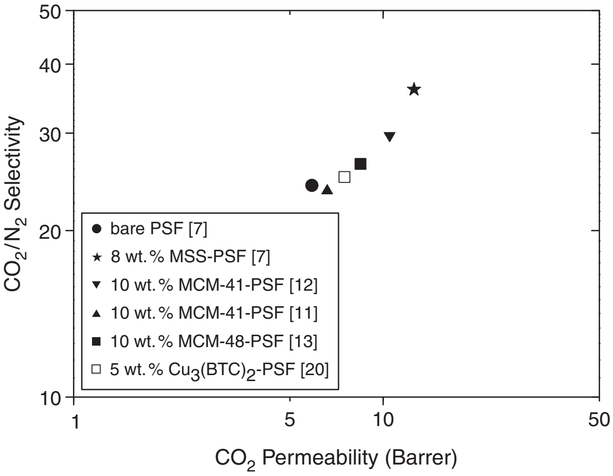


Fig. 5. CO_2/N_2 selectivity as a function of CO_2 permeability at 35°C for 8 wt.% MSS–PSF MMM compared with results from bare PSF and other authors.

As can be seen in Figs. 4 and 5, 8 wt.% MSS–PSF MMMs gave rise to the maximum H_2/CH_4 (79.2) and CO_2/N_2 selectivities (36.0). Concerning the permeability, 8 wt.% MSS–PSF MMM increased that for H_2 to 26.5 Barrer (compared to 11.8 Barrer for the bare PSF polymer). The CO_2 permeability increased from 5.9 (pure polymer) to 12.6 Barrer (8 wt.% MSS–PSF MMMs). The mesoporous phase may favor H_2 diffusivity over that of CH_4, while the increase of permeability is attributed to the disruption of polymer chain packing leading to an increase in polymer-free volume. Besides, compared to other MCM-41 [11,12] or MCM-48 [13] materials, the morphology of 2–4 μm spheres minimizes agglomeration and hence improves dispersability and interaction with the polymer [7]. Firstly, because the spherical shape limits the contact between silica particles, and secondly, due to the 2–4 μm spherical particles that provides a lower external surface area to volume ratio than that used in other reports (for instance, with 80 nm MCM-41 particles [12]).

In the case of 4 wt.% UZAR-S1-PSF MMM, while H_2 permeability exhibited a small decrease from 11.8 (bare polymer) to 11.5 Barrer, the H_2/CH_4 selectivity augmented from 58.9 to 69.2. This improvement is related to the six-membered rings that UZAR-S1 has along the [0 0 1] direction [8]: the molecular sieving ability of the sheets of UZAR-S1 is transferred to the composite membrane, favoring the transport of the smallest molecule (H_2). In accordance, a similar behavior took place for 5–10 wt.% swollen AlPO–6FDA copolyimide MMMs [14]: a reduction of CO_2 permeability from 84 to 51 Barrer was obtained, with improvement in selectivity from 8.28 of the pure polymer to 24.6 when 10 wt.% of the high aspect ratio material was added.

Both materials, MSSs and UZAR-S1, have BET areas of 1000 m^2/g [7] and 160 m^2/g [8], respectively. These specific surface areas are smaller than those of metal-organic frameworks, which present specific surface areas higher than 3000 m^2/g (MOF-5 = 3000 m^2/g, Cu-MOF = 3200 m^2/g, MOF-177 = 4500 m^2/g) [19]. Apart from the controlled porosity, which makes them good candidates for gas storage, some of them have good interaction with certain gases that may enhance the gas transport. MOF-5 has good affinity to CH_4 [19], MOF of copper and terepthalic acid (CuTPA) improve CO_2 solubility [10], $Cu_3(BTC)_2$ and $Mn(HCOO)_2 \cdot$ MOFs have also especial high sorption affinity for H_2 [20]. Cu–BPY–HFS shows affinity towards CH_4 [21] and ZIFs are also good to capture CO_2 from gas mixtures [22]. ZIFs provide Langmuir adsorption sites for CO_2 molecules, resulting in an increase in the MMM sorption with the filler loading [22]. In Figs. 4 and 5 membranes prepared with $Cu_3(BTC)_2 \cdot$ MOF and polysulfone are represented. They slightly improved the permselectivity compared to the corresponding values for pure polymer membranes [20]. Contrarily, MMMs prepared with 10 wt.% Cu–BPY–HFS and polyimide Matrimid® showed lower selectivity for H_2/CH_4 and CO_2/N_2 gas separation [21]. MMMs prepared with other MOF structures and polymers offer both high permeability and selectivity. For instance, MOF-5 embedded in Matrimid® improved H_2/CH_4 selectivity (from 110.9 for the pure polymer to 135.9) and H_2 permeability (from 24.4 to 29.9 Barrer) [19]. This same occurs for CO_2/N_2 selectivity (from 36.0 for the pure polymer to 39.6) and CO_2 permeability (from 9.0 to 11.1 Barrer). Other examples of higher permeabilities and selectivities compared with the bare polymer are those obtained with 15 wt.% CuTPA-PVAc MMMs for CO_2/N_2: the CO_2 permeability increased from 2.4 to 3.3 Barrer while selectivity from 32.1 to 35.4 [10].

4. Conclusions

We present a short literature review on special nanoporous fillers attempting to overcome the limitations of mixed matrix membranes. The incorporation of small amounts of ordered mesoporous silica spheres and delaminated microporous titanosilicate UZAR-S1 into commercial polysulfone membrane matrix has been successfully achieved. This led to promising results regarding the adhesion between the inorganic filler and the polymer matrix and the membrane gas separation performance.

Acknowledgements

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