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Microporous polymeric composite membranes with advanced film properties: Pore intercalation yields excellent CO_2 separation performance

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Abstract

Polymers of intrinsic microporosity (PIMs) are revolutionary gas separation materials because of their ultra-high permeability, but suffer from low gas pair selectivity (for example CO_2/N_2) and poor durability due to brittleness. Here we present a simple solution to these problems by blending PIM-1 with compatible polymer blend composed of PIM-1 and an ether side chain polyphosphazene (MEEP80), which possess better mechanical flexibility and higher CO_2/N_2 selectivity than the native PIM-1 while maintaining high CO_2 permeability. Under mixed gas test conditions, a blend of 25 wt% MEEP80 in PIM-1 has a CO_2 permeability of 2440 barrer and a CO_2/N_2 selectivity of 39 under mixed gas testing conditions, putting it among the best known polymers for CO_2/N_2 separation.

Introduction

Polymeric gas separation membranes have been studied extensively for gas separations but require further performance improvements for emerging industrial applications such as CO_2/N_2 separation for carbon capture from fossil fuel power generation.[1] An analysis by Merkel and co-authors suggests that a polymer membrane should have a CO_2/N_2 selectivity of at least 30 and a CO_2 permeance exceeding 2000 GPU in order to be considered economically viable in a two stage membrane process with an air sweep.[2] Achieving higher values of CO_2 permeance is desirable in order to process the enormous volume of flue gas that is emitted from fossil fuel power plants while minimizing the required membrane area.

In 2004, Budd et al. reported a new class of polymeric membranes known as polymers of intrinsic microporosity (PIMs) which have gained considerable attention for their ultra-high gas permeability.[3] The most extensively studied PIM, named PIM-1, was constructed from monomers which polymerized into a contorted backbone structure, leading to inefficient polymer chain packing and an intrinsic microporosity with unusually high free volume for a polymeric membrane.[4] With a CO_2 permeability of over 5800 barrer and a CO_2/N_2 selectivity of 16, PIM-1 sits just below the 2008 Robeson upper bound, which identifies the gas separation performance limit for pure polymeric materials.[5] This unprecedented permeability would make it a strong candidate for CO_2 capture, if not for several major drawbacks that are a result of its unique polymer structure. First, the average pore size of PIM-1 (~1 nm) leads to poor size discrimination between all gases compared to conventional glassy polymeric membranes such as Matrimid or polysulfone.[6] Second, a lack of hydrogen bonding between polymer chains results in a brittle film that is prone to cracking.

In recent years, many studies have been conducted with the goal of improving the gas selectivity of PIM-1.[7] Many of these studies involve post-functionalization to convert the nitrile groups of PIM-1 into functional groups such as carboxylic acids, amines, tetrazoles and amidoximes which can interact with CO_2.[8,9] Alternatively, PIM-1 has been blended with various polymers such as Matrimid, Torlon, polysulfone and polyionic liquids to improve the mechanical properties and/or gas selectivity.[10,11] Both functionalization and blending of PIM-1 have been shown to improve CO_2/N_2 selectivity, but it invariably comes at the expense of decreased free volume and CO_2 permeability. In addition, modified PIM-1 membranes were often still brittle and in most cases phase separation was reported due to poor blend compatibility.[10,12-14]

We report herein that an ether-functionalized polyphosphazene, PN[2-(2-methoxyethoxy)ethoxy](p-methoxyphenoxy) o-allylphenoxy}n (MEEP80), exhibited better phase compatibility across a larger composition range with PIM-1 compared to other polymers that have been blended with PIM-1. MEEP80 is an amorphous and rubbery polymer composed of a phosphazene backbone with a high concentration of ether side chains.[15,16] The phosphazene backbone provides high polymer chain flexibility and a low glass transition temperature, which are correlated with the enhancement of CO_2 permeability.[17] The polar interaction ability of the ether side chains of MEEP80 further contribute to high CO_2 permeability. Here, we chose MEEP80 for blending it with PIM-1 to enhance chain flexibility of the final composite membrane and for high selectivity of CO_2 over other other light gases. MEEP80 is a high-performance polymer material that also lies close to the Robeson upper bound for CO_2/N_2, but presents an opposite set of challenges compared to PIM-1. This material has a CO_2 permeability range of 400-500 barrer and a CO_2/N_2 selectivity over 30 at testing temperature of 30°C, but has a tacky, gel-like consistency. Blending the materials creates an ideal balance of the two, yielding a new Robeson upper bound polymer with improved selectivity for CO_2 compared to neat PIM-1, and with the distinct advantage of having excellent mechanical stability and durability.

Results and Discussion

PIM-1 was synthesized based on the low-temperature polycondensation reaction reported by Budd et al.[3] (NMR spectrum in Figure S1 and N_2 adsorption isotherm in Figure S2). MEEP80 was synthesized using the post-polymerization substitution of the chloro side groups of poly(dichlorophosphazene) ($NPCl_2$) with nucleophiles such as 2-(2-methoxyethoxy)ethanol (MEE), o-allylphenol and p-methoxyphenol (NMR shown in Figure S3).[18,19]

The 80 designation in MEEP80 refers to the 80 mol% substitution with the MEE group, with the phenolic groups making up the balance (Figure 1A). These phenolic groups improved the MEEP80 mechanical properties over 100% MEE-substituted polyphosphazene and increased its glass transition temperature (T_g).[20] While pure PIM-1 film coupons were brittle, MEEP80 is a semi-solid gel with more viscous than elastic characteristics (Figure 1B).[21] To form the blend polymer, both PIM-1 and MEEP80 were dissolved in chloroform at the desired composition, forming uniform and miscible solutions. Tetrahydrofuran was also found to be a suitable co-solvent. Solutions were poured into poly(tetrafluoroethylene) (PTFE) dishes and the solvent was allowed to evaporate at ambient conditions overnight. Cast films were removed from the PTFE dishes without any solvent treatment. Two different blend membranes were fabricated with 25 wt% and 50 wt% of MEEP80 in PIM-1 and are denoted as PIM-1/25 wt% MEEP80 and PIM-1/50 wt% MEEP80 respectively. All membranes were thermally treated at 70°C for 24 hours. Thermogravimetric analysis (TGA) of membranes resulted in two apparent decomposition temperatures corresponding to PIM-1 and MEEP80 (Figure S4). The onset of the higher decomposition temperature of PIM-1 decreased as the MEEP80 content increased. Blend membranes showed high thermal stability over 290°C, which is higher than most polymeric membranes.

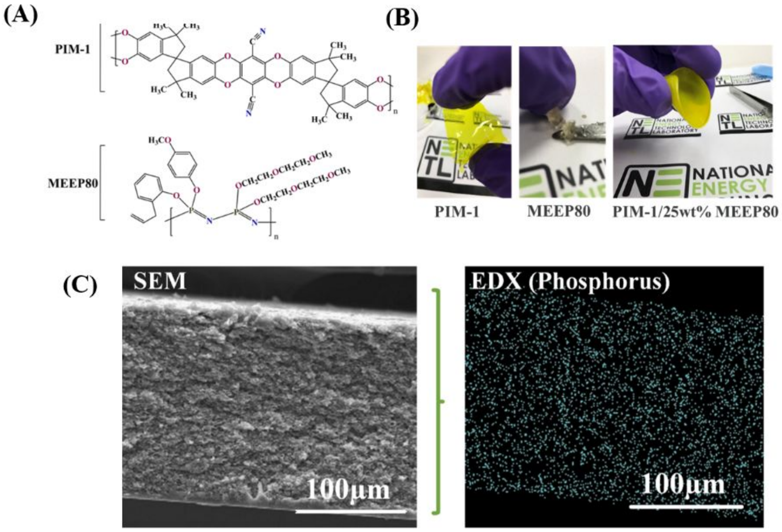

Figure 1. (A) Structures of PIM-1 and MEEP80, (B) photographs (left to right) of a brittle PIM-1 film, gel-like MEEP80 and a flexible PIM-1/25wt % MEEP80 films. (C) SEM image and EDX mapping of phosphorous in PIM-1/25 wt% MEEP80 showing the relatively uniform distribution of MEEP80.

Scanning electron microscopy (SEM) analysis and energy dispersive X-ray (EDX) mapping for phosphorous (present only in MEEP80) revealed that MEEP80 was distributed uniformly throughout the film cross-section with no visible defects or large-scale phase separation (Figure 1Cand Figure S5 and S6). This was true for both 25 and 50 wt% MEEP80 blends (Figure 1C, Figure S7 and S8).

Blend polymers, in general, can display morphological defects such as multiple phase transitions, polymer aggregation, and void formation due to phase incompatibility.[22] Differential scanning calorimetry (DSC) can be performed to evaluate polymer miscibility by comparing the glass transition temperatures (T_g) of the blend with those of the pure polymers. However, the T_g of PIM-1 is above its decomposition temperature (Figure 2A) and thus cannot be measured. The T_g analysis therefore depends entirely on comparison with pure MEEP80, which has a distinct T_g of -69.5°C. Blending PIM-1 into MEEP80 increased the T_g slightly to -66.3°C at 50 wt% MEEP80. The result suggests at least partial miscibility of MEEP80 with PIM-1 as chain interactions and entanglement decrease the MEEP80 chain mobility. Also secondary interactions such as Van der Waal`s forces may contribute to the T_g shift. We propose that the flexible MEEP80 chains can be intercalated within the relatively rigid and unconventionally large pores of the PIM-1 network, held together primarily by chain entanglement.[23,24]

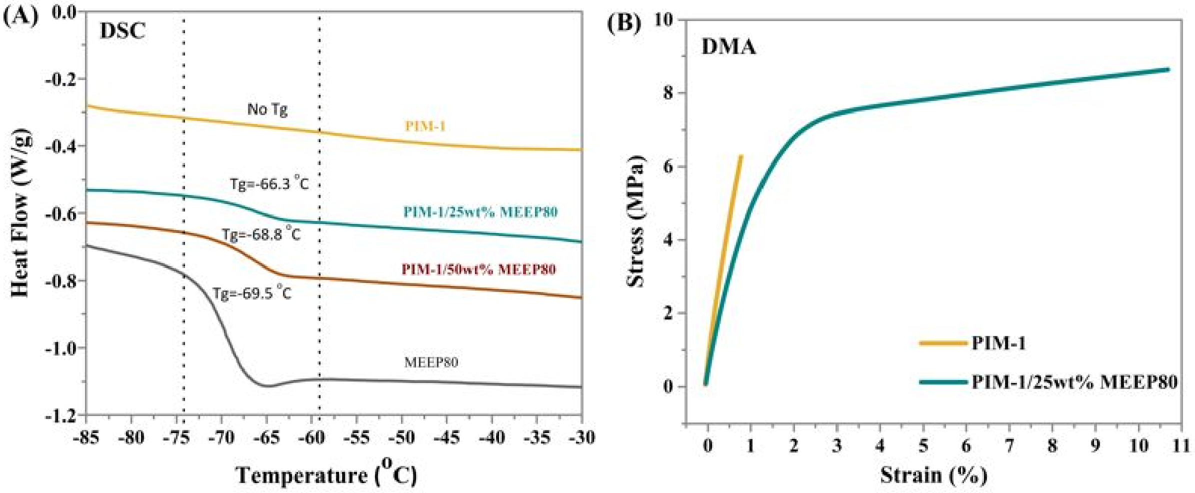

Figure 2. (A) DSC analysis of PIM-1, MEEP80 and blends of PIM-1/25 wt% MEEP80 and PIM-1/50 wt% MEEP80. (B) Tension tests for PIM-1 and 25 wt% PIM-1/MEEP80.

Further evidence of intermolecular interactions between PIM-1 and MEEP80 can be found in the FT-IR spectra. Incorporation of MEEP80 into PIM-1 resulted in increasing intensity of the P=N stretch at 1200 cm^{-1} on the MEEP80 backbone (Figure S9 and 10). Stretching of the dibenzodioxane C-O-C linkages in PIM-1 caused subtle shifts to higher frequency in a peak from 1008 to 1011 cm^{-1} and from 1261 to 1265 cm^{-1} with a higher MEEP80 concentration. This trend can be attributed to a molecular-level interaction between PIM-1 and MEEP80.[25]

A tensile test was performed using a dynamic mechanical analyzer (DMA) to quantitatively demonstrate the improvement in mechanical properties. While the Young`s modulus of PIM-1 (830 MPa) is higher than PIM-1/25 wt% MEEP80 (550 MPa), PIM-1 also has a very low strain to failure (< 1%) (Figure 2B) and it is a challenge to complete a measurement on the delicate thin film due to its brittleness. In contrast, the PIM-1/25 wt% MEEP80 membrane has a strain to failure of about 10.5%, giving it enough flexibility and durability to be handled and tested easily (Figure 1B).

Positron annihilation lifetime spectroscopy (PALS) was used to quantify the average inter-chain pore diameter and free volume of membranes by positronium (Ps) lifetime in the reported polymer dense films (see the SI for detailed procedure).[26] PALS measurements showed a clear trend in the pore size distribution of the polymers (Figure 3). The pore size distribution for PIM-1 is dominated by a peak with average pore diameter around 1 nm, while the pore distribution for MEEP80 is unimodal and centered around 0.7 nm. Incorporating MEEP80 into PIM-1 gradually decreased the intensity of the 1 nm pores with a modal shift towards the smaller pore size (Figure 3). At the same time, the 0.2 nm pores were eliminated. The results suggest that the flexible polyphosphazene can intercalate with the PIM-1, to some extent filling in the smaller void spaces. The prevalence of the 0.7 nm pores associated with MEEP80 was much more prominent for the 50 wt% blend compared to the 25 wt% blend, suggesting that for the 50 wt% composition a MEEP80-rich phase could be forming within the polymer once most of the smaller PIM-1 pores were filled. Since the blends do not present unimodal pore size distributions with proportionately changing average pore diameter it is difficult to assert that the PIM-1 and MEEP80 molecules have fully intertwined to form hybrid or blended voids.

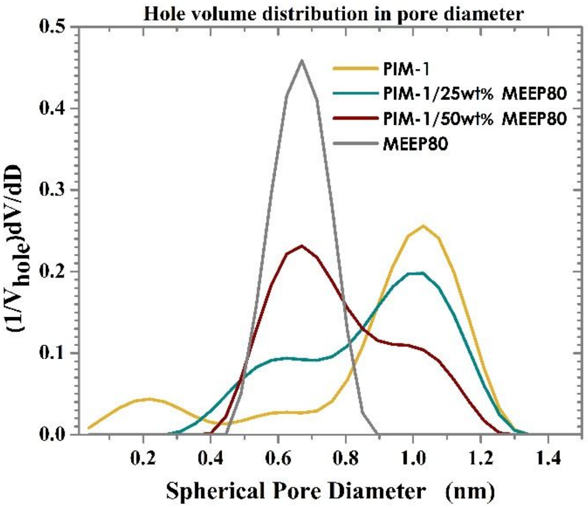

Figure 3. Pore diameter distribution measured by PALS for PIM-1, MEEP80, PIM-1/25 wt% MEEP80 and PIM-1/50 wt% MEEP80.

Pure gas permeability of the membranes was measured using an isochoric (constant volume) gas permeance test apparatus (described in the SI) at 40°C. Neat PIM-1 films have a pure gas CO_2 permeability of 5800 barrer with a CO_2/N_2 selectivity of 16, which is consistent with previous studies. PIM-1 blends with 25 wt% and 50 wt% MEEP80 showed significant improvement in the CO_2/N_2 selectivity (21 and 29, respectively) while the CO_2 permeability was decreased to 2450 and 2000 barrer, respectively (Figure 4A). In addition to CO_2 and N_2, permeability of CH_4, H_2, and O_2 was tested for neat PIM-1 and PIM-1/25 wt% MEEP80 membranes (Table S1). In the blended membranes, a larger loss in permeability for H_2 and O_2 compared to CO_2 and CH_4 is due to lower solubility (polarizability) of the former gases in the more rubbery MEEP80 component. The gas permeability decrease of the blend membranes was inevitable given the total free volume reduction but the CO_2 permeability remains significantly higher than most conventional polymer materials considered for carbon capture.[27,28]

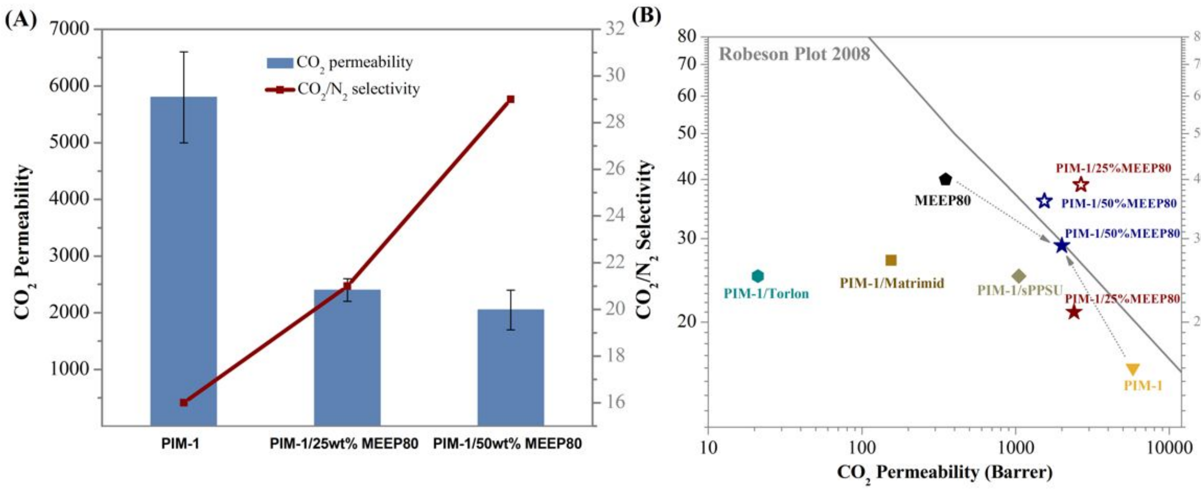

Figure 4. (A) Pure gas CO_2 permeability and CO_2/N_2 selectivity for neat PIM-1, and blends of 25 and 50 wt% MEEP80 in PIM-1. (B) CO_2 permeability and CO_2/N_2 selectivity of neat PIM-1(yellow

triangle, pure gas), neat MEEP80 (black pentagon, pure gas), and PIM-1/25 wt% MEEP80 (filled red star, pure gas; open red star, mixed gas) and PIM-1/50 wt% MEEP80 (filled blue star, pure gas; open blue star, mixed gas). [10,12,22,29]

The higher selectivity achieved by the blend membranes compared with neat PIM-1 was possible due to the incorporation of MEEP80, which possesses oligo(ethylene oxide) side groups that are known to interact well with CO_2.[30] Despite the weak size sieving ability of PIM-1, the improved selectivity was possible due to an increase in CO_2 solubility selectivity compared to the other non-polar gases evaluated here. The blends reported here exhibited a more significant improvement in CO_2/N_2 selectivity compared to other recent reports of PIM-1 based polymer blends.[27] In particular, PIM-1/50 wt% MEEP80 is the first blend polymer to fall on the Robeson upper bound for CO_2/N_2 separation.[27] Blends of PIM-1 with 50 wt% Torlon,[29] 50 wt% Matrimid,[12] 20 wt% sPPSU,[10], and 70 wt% Ultem[31] all resulted in a lower CO_2 permeability and CO_2/N_2 selectivity compared with PIM-1/MEEP80 blend membranes (Figure 4B).

The effects of aging on PIM-1/50 wt% MEEP80 was characterized by gas permeation testing up to 120 days from casting of the film (Figure S11). The CO_2 permeability of the blend polymer decreased by about 35% after 60 days, with only a slight reduction in CO_2/N_2 selectivity. The CO_2 permeability was unchanged after an additional 60 days, while the CO_2/N_2 selectivity again decreased slightly.

We also evaluated gas permeation properties of PIM-1/25 wt% MEEP80 and PIM-1/50 wt% MEEP80 blend membranes in mixed gas conditions ($CO_2/N_2/Ar$ 20:20:60) at 40 ^{o}C, 103 kPa CO_2 permeability of blend membranes increased to 2660 and 1540 with CO_2/N_2 selectivity of 39 and 36, respectively for PIM-1/25 wt% MEEP80 and PIM-1/50 wt% MEEP80 (Figure 4B).

In conventional glassy polymers, the mixed gas selectivity is lower than the pure gas selectivity due to the plasticization effect of CO_2.[32] But, in the case of high free volume glassy polymers like PIM, poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and thermally rearranged (TR) polymers, the mixed gas selectivity can be higher than the pure gas selectivity due to the preferential adsorption of the more condensable gas (in this case CO_2) in the free volume of the polymer.[13,33] Further evidence for this effect is shown in the CO_2 and N_2 isotherms (Figures S12 and S13). Henry`s law slope calculations of CO_2 and N_2 isotherms at 298K showed that neat PIM-1 possesses CO_2/N_2 solubility selectivity of 24 whereas the blend membrane PIM-1/25 wt% MEEP80 shows a higher CO_2/N_2 solubility selectivity of 42.

The adsorption of condensable gas also blocks the transport of the less condensable gas, similar to that of microporous materials, resulting in further improvement in selectivity. The fact that the mixed gas selectivity is enhanced even more for PIM-1/25 wt% MEEP80 than PIM-1/50 wt% MEEP80 is further evidence that this phenomenon is caused by the high free volume glassy (PIM-1) component of the blend.

Conclusions

This work presents a polymeric blend composed of PIM-1 and MEEP80 polyphosphazene which exhibits sufficient miscibility to make cohesive, mechanically robust membranes. The blend overcomes severe drawbacks that exist with both of the pure polymers, i.e. the brittleness of PIM-1 and the gel-like nature of MEEP80, yielding a composite which has excellent flexibility and toughness. These blends are soluble in common solvents, and hence are suitable for solution processing to form films and coatings for use in practical membrane applications. Most importantly, the high CO_2 permeability and CO_2/N_2 selectivity observed for PIM-1/25 wt% MEEP80 and PIM-1/50 wt% MEEP80 membranes make them the best PIM-1 blends reported to date for this gas separation, with performance on the Robeson upper bound for PIM-1/50 wt% MEEP 80 when tested in pure gas and above the Robeson upper bound for both blend compositions when tested in mixed gas. The materials are especially attractive for the application of post-combustion carbon capture where very high CO_2 permeability coupled with moderate CO_2/N_2 selectivity is desired in order to minimize the cost of an integrated carbon capture system.

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Disclaimer

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