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Gas transport in metal organic framework–polyetherimide mixed matrix membranes: The role of the polyetherimide backbone structure

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ABSTRACT

We report on how the morphology of the polymer matrix, *i.e.* amorphous vs. semi-crystalline, affects the gas transport properties in a series of mixed matrix membranes (MMMs) using $Cu_3(BTC)_2$ as the metal organic framework (MOF) filler. The aim of our work is to demonstrate how incorporation of $Cu_3(BTC)_2$ affects the polyetherimide matrix morphology and thereby highlighting the importance of selecting the appropriate polyetherimide matrix for mixed matrix membranes.

We used three amorphous poly(etherimide)s with very similar backbone structures. Polyetherimide ODPA-P1 was used as a linear flexible matrix, aBPDA-P1 is a non-linear rigid matrix and 6FDA-P1 was selected because the backbone structure is similar to ODPA-P1 but replacing the oxygen linker with two bulky $-CF_3$ groups results in a linear polymer with a low chain packing efficiency. Using an *in-situ* polymerization technique, up to 20 wt.% $Cu_3(BTC)_2$ could be homogenously dispersed in all three PEIs. The ODPA-P1 matrix crystallized when $Cu_3(BTC)_2$ was introduced as a filler. Gas permeation studies were performed by analyzing membrane performance using a 50:50 CO_2:CH_4 mixed gas feed. The presence of crystalline domains in ODPA-P1 resulted in a decrease in permeability for both CO_2 and CH_4 but the selectivity increased from 41 to 52 at 20 wt.% $Cu_3(BTC)_2$. The non-linear, rigid, aBPDA-P1 matrix remains amorphous when $Cu_3(BTC)_2$ is introduced. SEM images of the MMM cross-section revealed a sieve-in-a-cage morphology and at 20 wt.% $Cu_3(BTC)_2$, the permeation of both CO_2 and CH_4 increased by 68% thereby negating any change in selectivity. For 6FDA-P1 with 20 wt.% $Cu_3(BTC)_2$, only the permeability of CO_2 increased by 68% resulting in an increase in selectivity of 33%.

1. Introduction

3-D crystalline metal organic frameworks (MOFs) combined with polymeric matrices are prime candidates for separating gas mixtures [1]. The MOF filler contributes tunable chemistry [2,3], large surface area [4–6], adjustable pore size [7], selective affinity towards gas molecules [8–10], and high thermal stability [11]. These attributes make them attractive as additives for improving gas permeability and selectivity of polymeric membranes.

Although the gas separation properties of composite materials using inorganic fillers such as zeolites or sieves in a polymer matrix have been researched extensively, gas separation in polymer–MOF composites is less well understood [12,13]. So far, it is known that the low affinity of the polymer towards the inorganic filler generally results in the formation of non-selective voids at the polymer–filler interface, which in turn degrades the gas transport performance of the membrane [14]. Evidence of poor wetting by the polymer and debonding of the filler has been presented in scanning electron microscopy (SEM) images of membrane cross-sections [15]. In mixed matrix membranes (MMMs) using MOFs as fillers, the presence of organic ligands in MOFs is expected to

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lead to ‘better’ interfaces with the polymer matrix and therefore improve gas permeability and selectivity. Recent publications from our group and others have shown that increments in gas transport are indeed possible when modifying polymer matrices with MOFs [8,16,17,18,19]. But often, only an increase in permeability of the MMMs was observed without any increase in gas selectivity [6,20,21]. In general, the incorporation of MOFs in rubbery polymers leads to defect free MMMs but the high permeability of such polymers diminishes the contribution of the MOF fillers to gas transport [22,23]. In comparison, the use of high glass transition (Tg) rigid aromatic polyimides such as Matrimid® results in MMMs with a large number of non-selective voids at the interface [24,25]. Consequently, only an increase in gas permeability is obtained without any corresponding increase in selectivity.

Most research attention in the field of MOF–polymer membranes has focused on chemical modification and functionalization of the MOFs themselves in the hope of achieving higher affinities to specific gas molecules [10,26,27,28]. A systematic and detailed investigation into molecular aspects of the polymer matrix and subsequent changes in polymer morphology due to MOF inclusion has been noticeably absent. It must be noted that there have been some important contributions towards understanding polymer chain organization in the presence of zeolites such as the report published in 2004 by the group of Koros [14].

The most commonly found examples of polyimide matrices in literature are based on Matrimid™, P84, 6FDA-ODA and Ultem™. These matrices are known to have excellent gas-separation properties and they are solution processable. The lack of solubility of aromatic polyimides in common solvents is a reason for the commonly utilized two-step approach towards their synthesis. The first step involves preparing a solution of the soluble polyamic-acid intermediate. This polyamic acid is then cast as a film, the solvent is removed under vacuum at 60 °C and then subsequently the film is thermally imidized in steps up to 300 °C to form the insoluble polyimide. If the MOFs could be distributed homogenously in the polyamic-acid intermediate and the 3-D structure of the MOF could be maintained during thermal imidization, the field could be opened for a host of polyimide matrices that otherwise cannot be utilized.

Most reported mixed matrix membranes so far have been prepared using $Cu_3(BTC)_2$. The MOF $Cu_3(BTC)_2$ has a rigid 3D cubic structure with a main central cage having dimensions between 1 and 1.2 nm and intersectional pores with 0.6 nm tetrahedral side pockets. The main central cage and tetrahedral side pockets are connected by triangular windows of 0.35 nm that enable size sieving of gas molecules [18]. $Cu_3(BTC)_2$ has also been reported to exhibit a high affinity towards CO_2, which makes it attractive in separating CO_2 from CH_4 in natural gas feeds [29,30].

In terms of choosing polymer structures as the matrix, we have selected three poly(etherimide)s based on one all-aromatic diamine (1,4-bis(4-aminophenoxy) benzene, labeled **P1**) and 3 different dianhydrides (Scheme 1).

The ODPA-P1 polymer is an amorphous high performance all-aromatic polyetherimide that has been previously reported in literature [31]. In comparison to the other two polymers, this polymer is the most linear and most flexible and is anticipated to exhibit the highest chain packing density. In a past publication by Simons et al., the selectivity of CO_2 over CH_4 was reported to be ~50 at 5 bars for amorphous ODPA-P1 [32]. The linearity and conformational flexibility of this polymer is reflected in its ability to form crystal domains when cast and thermally imidized from polyamic acid solutions at concentrations of 10 wt.% or lower in NMP [33]. This makes it an ideal polymer matrix as it allows us to study the morphological changes induced by MOF inclusion and the subsequent changes in gas transport properties.

In contrast to ODPA-P1, 2,3′,3,4′-biphenyltetracarboxylic dianhydride or asymmetric BPDA and P1 (aBPDA-P1) results in a highly kinked and rigid polymer due to the asymmetry of the dianhydride moiety. The inability of this polymer to undergo crankshaft rotations around the C–C bond of the phenyl groups in aBPDA renders this polymer very rigid [34]. As far as we know, this polyetherimide has not been reported in the literature.

The incorporation of hexafluoroisopropylidene $(-CF_3)_2$ groups into the polymer backbone, as is the case for 6FDA-P1 (Scheme 1), restricts intra-segmental and inter-segmental mobility [35]. Also, the presence of hexafluoroisopropylidene bulky groups hinders effective chain packing leading to low polyetherimide densities [36]. In comparison to ODPA-P1, 6FDA-P1 has a larger free volume and higher conformational rigidity but is more linear than the highly kinked aBPDA-P1. Additionally, the presence of $-CF_3$ groups have been shown to help increase selective transport of gas molecules such as CO_2 [37] and interact (non-covalent) with the MOF filler [38].

In this research article, we will report on the thermo-mechanical and gas separation properties of three $Cu_3(BTC)_2$ modified polyetherimide model systems. Using a traditional 2-step polyetherimide synthetic procedure, we explored whether the addition of MOFs at the polyamic stage of synthesis is a viable alternative to using solutions of fully imidized polyimides. This synthetic method, if successful, will open up a wide range of otherwise insoluble aromatic polyimide matrix materials. The three poly(etherimide)s selected will aid in understanding the role of polymer morphology on gas permeation and gas separation when designing mixed matrix membranes.

2. Experimental

2.1. Materials

99.9% pure 3,3′,4,4′-oxydiphthalic dianhydride (ODPA) (99.9%) was purchased from TCI Chemical Industry Co. Ltd. 99.9% pure 4,4’-Hexafluoroisopropylidenebisphthalic dianhydride (6FDA) was purchased from Akron Polymer Systems. 95.0% pure 1,4-Bis(4-aminophenoxy) benzene (P1) was purchased from ABCR Inc. 2,3′,3,4′-Biphenyltetracarboxylic dianhydride (aBPDA) (99.9%) was generously donated by UBE Inc. Dry N-Methyl-2-pyrrolidone (NMP) (water content < 0.005%) was purchased from Acros Organics and used as received. Activated $Cu_3(BTC)_2$ MOF (also known as Basolite 300) was purchased from Sigma Aldrich and used as received.

2.2. Polyetherimide synthesis

The neat poly(etherimide)s based on ODPA-P1, 6FDA-P1 and aBPDA-P1 were synthesized using a standard two-step procedure *i.e.* synthesis of the polyamic acid followed by thermal imidization. The synthesis of ODPA-P1 is shown as an example in Scheme 2 [31].

A representative synthetic procedure is as follows: Synthesis of the ODPA-P1 polyamic acid. A 50 ml single neck flask fitted with an Argon inlet was charged with 0.747 g (2.55 mmol) of 1,4-bis (4-aminophenoxy)benzene (P1) and 5 ml of dry NMP. The mixture was stirred under argon atmosphere until all the diamine monomer dissolved. The polymerization was initiated by adding 0.793 g (2.55 mmol) of 3,3′,4,4’-oxydiphthalic dianhydride (ODPA). The concentration of monomers in NMP for all polyamic acid intermediates was 22 wt.% in NMP. The solution was left to stir overnight for polymerization to be complete. Prior to film casting, all polyamic acid solutions were diluted to monomer concentration of 18 wt.% of NMP.

Synthesis of 20 wt.% $Cu_3(BTC)_2$ ODPA-P1 polyamic acid