



Asymmetric hollow fiber membrane coated with polydimethylsiloxane–metal organic framework hybrid layer for gas separation



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ABSTRACT

This study presents an alternative approach to improve the gas separation performance of conventional asymmetric membranes. For the first time, multicomponent composite/hybrid asymmetric membrane was prepared by unifying two prominent concepts in gas separation membranes: (1) sealing or caulking asymmetric membrane imperfections by means of coating a highly permeable polymer layer, and (2) the incorporation of selective inorganic particle in polymer matrix generally known as the mixed matrix membrane. Asymmetric hollow fiber membranes (polysulfone (PSF)) was externally coated by polydimethylsiloxane (PDMS) solution containing suspended $\text{Cu}_3(\text{BTC})_2$ metal organic framework (MOF) by dip-coating technique. FESEM–EDS mapping confirmed the increase in $\text{Cu}_3(\text{BTC})_2$ adherence with increasing number of coating. The pure gas permeation experiment with CO_2 , N_2 and CH_4 corroborated the contribution of $\text{Cu}_3(\text{BTC})_2$ particle to the overall composite/hybrid membrane performance. The gas permeation rates were increased with increasing number of PDMS– $\text{Cu}_3(\text{BTC})_2$ coating applied. CO_2 permeance increased from 69.7 to $109.2 \times 10^{-6} \text{ cm}^3 (\text{STP})/\text{cm}^2 \text{ s cmHg}$ after 5 consecutive coatings. In addition, the CO_2/CH_4 and CO_2/N_2 selectivities were found to be increased as well. $\text{Cu}_3(\text{BTC})_2$ contributed to higher affinity toward CO_2 due to the coordinatively unsaturated copper sites in its crystal network, which provide exceptionally high adsorptive capability for polar molecules, hence resulted in the increase of the overall selectivities and gas permeation rates across the membrane. Further development based on this study will create vast opportunities for future improvement on any commercially available gas separation membranes by implementing the method described herein.

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1. Introduction

Polymeric membrane with asymmetric structure has been acknowledged as the most preferred material for the industrial membrane based gas separation applications. Gas transport through asymmetric polymeric membranes are predominantly determined by the characteristics of the dense skin layer of an asymmetric membrane. The dense skin layer of asymmetric membrane is integrally formed on a more porous substructure from the same material through phase inversion process. Although asymmetric membranes with extremely thin skin layer (less than 100 nm) can be attained by the phase inversion process, the formations of defects such as pinholes are almost inevitable. Membranes suffered with defective skin would exhibit poor gas selectivities since the gases will travel through the pinholes non-selectively.

In 1980s, Monsanto's researchers patented a caulking technique by means of coating a highly permeable polymer layer on the membrane defective skin [1]. As a result, the selectivity of the membrane can be recovered near to its intrinsic performance. Ever since, the caulking technique has been industrially implemented to coat the surface of asymmetric membranes by using a diluted silicone rubber, namely polydimethylsiloxane (PDMS), typically 3% w/w in alkane solvent (i.e., *n*-pentane, *n*-hexane). Despite of having improved selectivity, the membrane performance is essentially bounded by the intrinsic performance of the membrane material itself.

Although the use of asymmetric polymeric membranes in the gas separation industry has been conceded as an effective technology, yet the industry persistently demands for a better membrane with higher separation performance. However, it is unlikely that the performance of the currently applied polymeric membranes could be further increased if no drastic change is made on the essence of the membrane material itself. Numerous strategies have

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been proposed, including the modification of polymer structures and polymer blending in order to attain novel materials with superior separation characteristics [2,3]. Unfortunately, synthesizing new materials or modifying the structure of existing polymeric materials only resulted in marginal changes from the intrinsic performance where a trade-off relationship between the permeability and selectivity still exists [4,5].

In view of this problem, membranologists inferred that the incorporation of fillers into polymer membrane matrix would yield a new class of membrane with significantly improved gas separation performance and physical stability. This approach, which known as mixed matrix membrane (MMM) is believed to be a viable mean to overcome the permeability and selectivity trade-off relationship [6]. Mixed matrix membranes can, apart from with inorganic fillers, also be formed with organic or hybrid organic–inorganic fillers [7]. Since the last decades, highly selective inorganic particles such as zeolite and carbon molecular sieves are of great interest to be chosen as the MMM dispersed phase [8].

Recent development has shown considerable attention in synthesizing MMM containing relatively new class of adsorptive fillers, namely, metal organic framework (MOF). MOF is crystalline organic–inorganic hybrid compounds made up of metal ions (clusters, chains, layers or 3D arrangement) bonded to organic ligands which comprises of complexing segments (carboxylates, phosphonates, *N*-containing compounds) via strong ionocovalent or dative bonds [9]. There are innumerable types of MOFs since these crystal nanostructures can be engineered from almost all known elements in the periodic table. Therefore the architectural design of MOFs can be tailored into various pore structures with different functionalities. MOF has recently emerged as an important material for catalyst, adsorption, gas storage, and separation [10–12]. One of the most prominent MOFs is $\text{Cu}_3(\text{BTC})_2$, also known as HKUST-1. The key structural characteristic of $\text{Cu}_3(\text{BTC})_2$ is a copper dimer with a Cu–Cu distance of 2.63 Å. $\text{Cu}_3(\text{BTC})_2$ pore structure consists of two types of cages: large main cavities, connected to each other by nearly square windows of ca. 9 Å edge, and small octahedral-shaped pockets. There are eight pockets per unit cell, accessible from the main cavities through small triangular windows whose inscribed circle is approximately 4.6 Å in diameter. Due to its large pore volume as well as the presence of coordinatively unsaturated copper sites in its crystal network, it provides exceptionally high adsorptive capability for polar molecules, especially toward CO_2 [10]. CO_2 adsorption quantities of $\text{Cu}_3(\text{BTC})_2$ were reported to be 1.2 mmol/g at 1 bar [11], and can reach up to 10 mmol/g at 8 bar and 25 °C [12]. Due to these aforementioned key features, $\text{Cu}_3(\text{BTC})_2$ is recognized as one of the most sophisticated MOFs utilized in the development of MMM for gas separation.

Car et al. [13] studied the properties of $\text{Cu}_3(\text{BTC})_2$ MMM prepared from rubbery (PDMS) and glassy polymer (polysulfone, PSF) and found that they behaved differently in each matrix. $\text{Cu}_3(\text{BTC})_2$ can be loaded to PDMS in much higher amount than in PSF due to the flexibility of PDMS chain. Defect-free PDMS– $\text{Cu}_3(\text{BTC})_2$ can be obtained up to 30% loading, whilst only 5% loading for PSF– $\text{Cu}_3(\text{BTC})_2$ MMM. Addition of $\text{Cu}_3(\text{BTC})_2$ in both matrix resulted in improved permeability and selectivity.

More recently, Basu et al. [14] prepared asymmetric MMM from Matrimid® and Matrimid®/polysulfone blend comprising $\text{Cu}_3(\text{BTC})_2$ MOF for gas separation. The selectivity and permeance of the $\text{Cu}_3(\text{BTC})_2$ -filled membranes were increased with increasing $\text{Cu}_3(\text{BTC})_2$ loading. The incorporation of $\text{Cu}_3(\text{BTC})_2$ particle also enhanced the thermal and mechanical stability of the membrane. However, high amount of sieve filler is required in order to give profound impact on the membrane separation properties (>10 wt.%) [15]. The formation of agglomerations and interfacial voids upon the inclusion of inorganic particle at high loadings (>30 wt.%) have been constantly reported to cause unsavoury

separation performance in glassy polymers [13,16]. In addition, if the MMM were to be tailored into asymmetric form, the incorporation of inorganic fillers are only effective if the fillers are embedded in the dense skin region of the membrane, while maintaining perfect adhesion to the polymer matrix. Although Chung's research group [17,18] have reported a compelling phenomenon where elongation stretch during hollow fiber spinning might facilitate the particles migration toward the bore and shell sides of the hollow fiber, it is still impossible to control the complete embedment of the particles in the dense skin layer region, unless dual layer hollow fiber MMM is fabricated, wherein inorganic particles can be exclusively incorporated in the sheath layer [19].

In this study, we aim to introduce a facile method to form a mixed matrix composite membrane which can be formed on any as-fabricated asymmetric membranes in order to improve the performance of the membrane beyond its intrinsic level. This approach involves the combination of two important concepts: (1) sealing or caulking asymmetric membrane imperfections by means of coating a highly permeable polymer layer, and (2) the incorporation of selective or adsorptive inorganic particle in polymer matrix known as mixed matrix membrane. The method involves a coating procedure wherein absorbent inorganic filler will be accommodated within the coating layer as illustrated in Fig. 1. Not only the coating layer serves to caulk minor surface imperfections possibly present on the membrane surface, it will also provide adequate protection for the membrane during the entire handling and testing processes [1]. In addition, due to the embedment of adsorptive inorganic filling in the coating layer, the overall separation capability of the membrane could be further enhanced due to the adsorptive and selective nature of the filler. Asymmetric hollow fiber membrane was spun by dry-jet wet phase inversion technique and subsequently subjected to coating treatment. The membrane was later characterized by pure gas permeation test. The morphology and the dispersion of inorganic particles in the coating layer was studied by FESEM as well as with the aid of EDS mapping analysis.

2. Experimental

2.1. Materials

Polysulfone (PSF Udel-P3500) was chosen as polymer matrix phase of the hollow fiber membrane. PSF in pellet form was supplied by Amoco Chemicals. *N,N*-dimethylacetamide (DMAc) and ethanol were supplied by Merck, while tetrahydrofuran (THF) from QReC. The coating material, polydimethylsiloxane (PDMS, Sylgard® 184) was procured from Dow Corning. It was supplied as two part liquid component kits: an elastomer base and a curing agent. Hexane (Sigma–Aldrich, Germany) was used as the solvent in the preparation of PDMS coating solutions. $\text{Cu}_3(\text{BTC})_2$ (Copper benzene-1,3,5-tricarboxylate) was acquired from Sigma Aldrich (Germany) under the trade name Basolite® C300. Some representational properties of the filler can be found in Table 1. The $\text{Cu}_3(\text{BTC})_2$ was dehydrated at 150 °C for 12 h before usage.

2.2. Methods

2.2.1. Fabrication of hollow fiber membrane

The PSF spinning dope was formulated to consist of 30% w/w PSF, 35% w/w DMAc, 30% w/w THF, and 5% w/w ethanol. Dope solution preparation procedure can be found elsewhere [20]. The hollow fiber membrane was fabricated in our laboratory using a custom built spinning system. The hollow fiber was spun by force-convective dry-wet spinning process according to the procedure described in our recent publication [21]. In brief, the prepared

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