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Hybrid polymer/MOF membranes for Organic Solvent Nanofiltration (OSN): Chemical modification and the quest for perfection

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ABSTRACT

One of the main challenges in the field of Organic Solvent Nanofiltration (OSN) is to improve the selectivity of membranes, allowing the separation of closely related solutes. This objective might be achieved by constructing membranes with uniform porous structures. Hybrid Polymer/Metal Organic Framework (MOF) membranes were prepared by in-situ growth (ISG) of HKUST-1 within the pores of polyimide membranes. To improve the performances of ISG membranes, chemical modification was performed. Aryl carboxylic acid moieties were introduced to polyimide P84 ultrafiltration membranes allowing coordination of the HKUST-1 directly on to the polymer. Chemically modified ISG membranes outperformed non-modified ISG membranes in both solute retentions and permeance. Retentions of polystyrene solute in acetone were used to calculate theoretical pore size distributions for each of the membranes tested. It was found that the chemically modified ISG membrane had he narrowest calculated pore size distribution.

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1. Introduction

Organic Solvent Nanofiltration (OSN) is an emerging pressure driven separation methodology that uses semi-permeable membranes to selectively separate on a molecular basis [1,2]. Polymeric integrally skinned asymmetric (ISA) membranes fabricated via immersion precipitation phase inversion remain the most commonly used membranes in OSN processes [2]. Polymeric ISA membranes have a number of advantages, including flexibility and ease of production. The properties of polymer membranes can be altered by modifying the phase inversion process [3], however the structure of the selective layer of ISA membranes cannot yet be designed at a molecular level. ISA membranes will always exhibit a pore size distribution, rather than a single regular pore size [4]. To introduce more molecular order to the structure of polymeric membranes, hybrid membranes containing Metal Organic Frameworks (MOFs) have been developed.

Recent developments in the fabrication of hybrid polymer/MOF membranes have led to the development of these kinds of membranes for gas separations and OSN processes. Mixed matrix membranes (MMM) have been shown to improve the permeance and selectivity of polymeric membranes above the Robeson upper bound for gas separations [5–12]. MMMs have also been used for OSN processes, using various MOF particles embedded in the selective layer of thin film composite (TFC) membranes [13], and HKUST-1 particles dispersed in integrally skinned asymmetric (ISA) polymer membranes [14]. While MMMs have been shown to improve the retention properties of polymer membranes further improvements were made using *in-situ* growth (ISG) membranes.

In-situ growth (ISG) is a hybrid membrane fabrication methodology which has been used to produce hybrid polyimide/HKUST-1 membranes for OSN [14]. ISG membranes have been shown to improve solute retentions and flux decline properties above that of pure polymer membranes and mixed matrix membranes (MMMs) for OSN. ISG membranes have also been used for gas separations [15–17]. However there is scope for further improvement of the performances of ISG hybrid membranes through modification of the polymer matrix. Chemical modification techniques have been successfully applied to MMMs containing inorganic particles to improve the interaction between the polymer and inorganic phases of the membranes for gas separations [18,19] and OSN [13,20].

Functionalization of polymers by small-molecule organic chemistry reactions is a vibrant field of research and has attracted

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Abbreviations: CMA, Chemical modification agent; HKUST, Hong Kong University of Science and Technology; HDA, Hexane-1,6-diamine; ISA, Integrally skinned asymmetric (membrane); ISG, In-situ growth; MMM, Mixed matrix membrane; MOF, Metal Organic Framework; OSN, Organic Solvent Nanofiltration; SEM, Scanning Electron Microscopy; TFC, Thin film composite

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great attention lately due to an increasing number of novel potential applications [21]. Post-polymerization chemical modification can be used to incorporate functionalities into existing polymer chains and networks. This approach circumvents a number of problems associated with direct polymer synthesis and enables the creation of polymeric systems which may be difficult or impossible to produce otherwise. Examples include post-polymerization modifications to create aliphatic poly(carbonate)s for biomedical applications [22], imprinted materials for advanced separations [23] or functional polymers featuring labile groups such as alkynes or thiols [24]. In order to achieve improved solute retentions using ISG membranes, chemical modification agents were used with a view to reducing the voids/defects between polymer and the MOF crystals. In this paper chemical modification has been applied to encourage the growth of MOF (HKUST-1) directly on the walls of the pores. This is achieved through the incorporation of benzene tri-carboxylate functional groups into the polyimide polymer chain.

The ISG membrane fabrication methodology was developed to modify the pores of ISA polymer membranes, intending to create membranes with more regular, predictable porous structures. Due to the phase inversion process, which is the most common methodology used to produce polymer membranes for OSN [2], ISA polymer membranes always exhibit a distribution of pore sizes [4,26–28]. Introduction of HKUST-1 to hybrid polymer/MOF membranes is meant to augment the structure of the separation layer of the membrane and specifically to narrow its pore size distribution. Narrower pore size distributions could lead to sharper molecular weight cut-off (MWCO) curves, which would allow for better separations between molecules close in molecular weight.

It is difficult to directly measure, on a nanoscale, the pores in polymer materials experimentally. Recently methodologies have been developed, including Positron Anilhilation Lifetime Spectroscopy (PALS) [29,30] and nanoprobe imaging [31]. However these methods are relatively unproven, and require expensive equipment and complicated techniques. Alternatively derivative methodologies can be employed, using filtration data to estimate pore size distributions. This paper uses experimental data to model the pore size distributions of the membranes in order to measure the effect MOF addition has on the pore size distribution of hybrid polymer/MOF membranes. Transport phenomena through membranes have been described using four kinds of models: irreversible thermodynamics, solution–diffusion, pore-flow and solution–diffusion with imperfections (SDI). The solution-diffusion and pore flow model are both widely used for describing transport through nanofiltration membranes [50]. In this paper the pore-flow model was chosen to study the effect chemical modification and the presence of MOFs on the pore size distribution of hybrid polymer/MOF membranes. Using the rejection of polystyrene solutes log-normal pore size probability functions were calculated for each of the membranes tested in this paper.

This paper uses the same pore flow model to predict the rejection and permeance of defect free HKUST-1 films. These calculations will evaluate how close ISG membranes have come to the performance of ideal MOF films.

2. Experimental

2.1. Materials

Polypropylene non-woven backing was supplied by Viledon, Germany. Polyimide (PI) polymer (P84) was purchased from HP Polymer GmbH, Austria. Solvents used for membrane preparation and membrane testing including isopropanol, acetone, DMF, 1,4-dioxane, ethanol (99.7%) and polyethylene glycol (MW 400) (PEG-400) were obtained from VWR international. Hexane-1,6-diamine for crosslinking was purchased from Sigma Aldrich. Copper nitrate trihydrate and 1,3,5-benzenetricarboxylic acid used to fabricate ISG hybrid polymer/MOF membranes were also purchased from VWR international. 1,2,4-Benzenetricarboxylic anhydride chemical modification agent (CMA) was purchased from Sigma-Aldrich. Polystyrene markers for solute rejection evaluation were purchased from Agilent Technologies, UK. Novatex 2471 Polypropylene non-woven supports were supplied by Freudenberg Filtration Technologies. All the chemicals were used as received without any further purification.

2.2. Membrane preparation

2.2.1. Preparation of ultrafiltration membranes

Polyimide P84 ultrafiltration (UF) membranes were produced via phase inversion. UF membranes were fabricated via the methodology used to produce dense UF membranes previously described by the authors [14]. Dope solutions were formed by dissolving 24 wt% of polyimide polymer in DMF. The P84 was dissolved using a magnetic stirrer at room temperature, in a sealed container to ensure no moisture was absorbed into the solution. The dope solutions were cast onto polypropylene non-woven supports using a casting knife set to a thickness of 250 μm, in an environment with a temperature of 15 °C and a humidity of 50–60%. The membranes were then precipitated from solution via immersion in water. The membranes were subsequently placed in isopropyl alcohol (IPA) to remove water from the polymer matrix. The membranes were then submerged in 30 g L^{-1} solutions of 1,6-hexamethylenediamine (HDA) in IPA for 20 h in order to crosslink the polymer chains, improving the chemical resistance of the membranes. After crosslinking, the membranes were washed with IPA to remove excess crosslinking agent. Before testing, the membranes were conditioned with a PEG400:IPA (60:40 v/v) solution for 12 h.

2.2.2. Membrane chemical modification

Chemical modification was performed on UF membranes using the chemical modification agent (CMA) 1,2,4-benzenetricarboxylic anhydride in order to introduce a tricarboxylate functional group into the membrane matrix. Crosslinked polyimide P84 membranes contain amides, which can readily react with anhydrides. When the anhydride reacts with the amide the anhydride ring opens up and attaches to the polymer matrix, while also forming a carboxylate functional group available to react with copper ions to begin forming the building blocks of HKUST-1 within the membrane.

Prior to chemical modification the crosslinked UF membranes were washed with DMF to remove IPA from the pores. The membranes were placed in solutions of 1,2,4-benzenetricarboxylic anhydride in DMF for 20 h at 25 °C. The amount of CMA added to the solutions was based on the assumption that each polymer unit contains four sites available to react with the 1,2,4-benzenetricarboxylic anhydride molecule (see Fig. 1). For each membrane one equivalent of CMA was added using 10 g L^{-1} solutions of 1,2,4-benzenetricarboxylic anhydride in DMF, with the volume of solution adjusted according to the mass of membrane. After the reaction each membrane was repeatedly washed with DMF to remove any unreacted CMA from the polymer matrix.

2.2.3. Preparation of hybrid polymer/metal organic membranes

ISG hybrid polymer/MOF membranes were prepared by immersing the polymer UF membranes, both modified and unmodified, into a fresh mixture of copper nitrate (0.86 M EtOH solution) and 1,3,5-benzenetricarboxylic acid (0.40 M DMF solution)

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