The Development of Hybrid Polymer-Metal Organic Framework Membranes for Organic Solvent Nanofiltration

By

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A thesis submitted for the degree of Doctor of Philosophy of Imperial College London and the Diploma of Imperial College London
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Abstract

The most common membranes used for organic solvent nanofiltration (OSN) are integrally skinned asymmetric membranes formed via the immersion precipitation phase inversion process. These membranes are flexible, durable and easy to produce. However control of the porous properties of these membranes is not possible on a molecular level. Integrally skinned asymmetric membranes always exhibit signs of a pore size distribution, which leads to rejections not being optimum. Metal organic frameworks (MOFs) were added to polymeric OSN membranes in an attempt to improve the control over porous properties and separation properties above those achievable using integrally skinned asymmetric polymer membranes.

MOFs are crystalline materials with regular porous structures. MOFs have been used for gas separation purposes. This thesis describes the fabrication of hybrid polymer/MOF membranes for OSN applications. MMM fabrication is the tradition approach to create a hybrid polymer/MOF membrane, and contains discrete particles of MOF in a continuous polymer phase. The advantage of MMMs is that they are easy to produce; however, due to the discrete nature of the MOF in the membrane; the permeation of molecules through the membrane is not completely controlled by the MOF. MMMs were shown to have little difference in performance to polymer nanofiltration membranes for OSN.

In order for the MOF to exhibit more control over the permeation properties of membranes, in-situ growth (ISG) membranes were developed, whereby MOF material is grown within the pre-existing pores of polymer membranes. Using the MOF HKUST-1 and ultrafiltration polyimide supports ISG membranes were produced and were shown to outperform MMMs in terms of both solute retention and flux decline. Energy-dispersive X-ray spectroscopy (EDX) was used to reveal the distribution of HKUST-1 throughout ISG membranes, which was found to be even across the surface and throughout the cross-section, showing that a continuous phase of MOF had been grown.
Acknowledgments

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(or maybe I would I don’t know)

I love you with all my heart.
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<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>APTMS</td>
<td>3-Aminopropyl trimethoxysilane</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflection Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BTC</td>
<td>Benzene tricarboxylic acid</td>
</tr>
<tr>
<td>CMA</td>
<td>Chemical modification agent</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>HDA</td>
<td>Hexamethylenediamine</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>HKUST</td>
<td>Hong Kong University of Science and Technology</td>
</tr>
<tr>
<td>HPB</td>
<td>Hexaphenylbenzene</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropanol/isopropyl alcohol</td>
</tr>
<tr>
<td>IRMOF</td>
<td>Isoreticular Metal Organic Framework</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ISA</td>
<td>Integrally skinned asymmetric</td>
</tr>
<tr>
<td>ISG</td>
<td>In-situ growth</td>
</tr>
<tr>
<td>Mac-RO</td>
<td>Membrane assisted crystallisation - reverse osmosis</td>
</tr>
<tr>
<td>MMM</td>
<td>Mixed matrix membrane</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal Organic Framework</td>
</tr>
<tr>
<td>MPD</td>
<td>m-Phenylenediamine</td>
</tr>
<tr>
<td>MSTFA</td>
<td>N-methyl-N-(trimethylsilyl)-trifluoroacetamide</td>
</tr>
<tr>
<td>MW</td>
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</tr>
<tr>
<td>MWCO</td>
<td>Molecular weight cut-off</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>OSN</td>
<td>Organic solvent nanofiltration</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PBI</td>
<td>Polybenzimidazole</td>
</tr>
<tr>
<td>PCP</td>
<td>Porous coordination polymers</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<td>PEEK</td>
<td>Polyether ether ketone</td>
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<td>PEG</td>
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<td>Polyimide</td>
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<td>Polymer with intrinsic microporosity</td>
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<td>PSf</td>
<td>Polysulfone</td>
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<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
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<tr>
<td>PyDC</td>
<td>Pyridine-3,5-dicarboxylate</td>
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<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>SBU</td>
<td>Second building unit</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TFC</td>
<td>Thin film composite</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<td>Trimesoyl chloride</td>
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<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-Visible</td>
</tr>
<tr>
<td>XRPD</td>
<td>X-ray powder diffraction</td>
</tr>
<tr>
<td>ZIF</td>
<td>Zeolitic imidazolate framework</td>
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### Nomenclature

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<tr>
<th>Symbol</th>
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<tr>
<td>A</td>
<td>Area</td>
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</tr>
<tr>
<td>C</td>
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</tr>
<tr>
<td>d</td>
<td>Molecular diameter</td>
<td>m</td>
</tr>
<tr>
<td>D</td>
<td>Diffusivity</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>Jᵥ</td>
<td>Flux</td>
<td>L m⁻² h⁻¹ (SI units: m³ m⁻² s⁻¹)</td>
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<tr>
<td>k</td>
<td>Permeability Coefficient</td>
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<td>Kₛ</td>
<td>Sorption Coefficient Constant</td>
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Chapter 1

1. Research Motivation and Thesis Overview

Organic solvent nanofiltration (OSN) is an emerging pressure driven separation methodology that uses semi-permeable membranes to selectively separate on a molecular basis. OSN membranes are fabricated to be stable in the presence of organic compounds e.g. alcohols, aromatic compounds and oligomers. Polymeric integrally skinned asymmetric (ISA) membranes fabricated via immersion precipitation phase inversion remain the most commonly used membranes in OSN processes[2]. The simplified production methodologies of these membranes lead to low manufacturing costs[2]. ISAs are also designed to be flexible so they can be used within membrane modules e.g. spiral wound membrane modules[2]. Despite these advantages, the porous structure of ISA membranes currently cannot be accurately controlled. The structure of the selective layer of ISA membranes cannot be designed on a molecular level, and these membranes will always exhibit a pore size distribution, rather than a single regular pore size[3]. To introduce more molecular order to the structure of polymeric membranes this thesis explores a number of fabrication methodologies to produce hybrid polymer/metal organic framework (MOF) membranes.

MOFs are crystalline materials, consisting of metal ions or metal ion clusters, connected by organic ligands to form a continuous regular network[4, 5]. Many MOFs are highly porous[5-8] and thus are suitable for separation processes. In fact MOFs have been extensively used in gas separation processes, both as stand-alone membranes and as hybrid polymer/MOF membranes. MOFs have regular, repeating patterns of pores, which can be predicted and controlled depending on the choice of organic ligand. Pure MOF membranes however are expensive to produce, brittle and unable to be scaled up for use in modules. There has been much research conducted into the fabrication of membranes that combine the flexibility of polymer membranes, while incorporating the selective properties of inorganic/crystalline materials, such as MOFs. Hybrid polymer/MOF membranes known as mixed matrix membranes (MMMs) have been extensively used in gas separations. There has been very little research into the application of hybrid polymer/MOF membranes within OSN processes.

Chapter 2 serves as a literature review on the fabrication, application and characterisation of membrane technology, with a specific focus on OSN applications and the scope for the use of hybrid polymer/MOF membranes in these applications. The shortcomings of the immersion precipitation phase inversion process are discussed in detail. The development of hybrid polymer/inorganic membranes is also discussed including the materials that have been used to date. The remaining chapters of the thesis detail the design of hybrid polymer/MOF membranes for OSN, developed using fabrication methodologies utilised for gas separations.

For each membrane fabrication methodology used, the rejection and permeance performances are related to the morphology and structure of the membranes. Several characterisation methodologies are employed to explore the physical and chemical nature of the membranes. To achieve MOF mediated separations, and truly control the selective nature of separations, it is desired to fabricate defect free membranes, with MOF material present at the membrane surface. Therefore this thesis will not only describe the design, fabrication and application of hybrid membranes for OSN, but discuss how the fabrication methods employed lead to a certain membrane structures and in turn how these structures influence the performances of these membranes.
The most basic form of hybrid polymer/MOF membranes, MMMs are composed of discrete MOF particles in continuous polymer films. The fabrication and application of MMMs, comprised of MOFs embedded in the polymer matrix of ISA membranes, is explored in Chapter 3. This represents the simplest fabrication methodology available to produce hybrid membranes, and the methodology has been applied to membranes used in gas separations to improve permeance and selectivity performances. Chapter 3 addresses issues frequently associated with the formation of MMMs, such as non-selective voids, while exploring the influence discrete particles of MOF embedded in polymer membranes can have on separation performances.

Chapter 4 compares the commonly used mixed matrix membrane fabrication methodology and a novel approach for producing hybrid polymer/MOF membranes, in-situ growth (ISG). Using polymer ISA polyimide P84 membranes, hybrid polymer/MOF HKUST-1 membranes were produced and tested in OSN conditions. The ISG fabrication methodology is designed to create a continuous phase of MOF throughout a polymer support membrane. The structures of ISG membranes are compared to MMMs, and the different structures are related to performances of the membranes.

Chapter 5 details a number of methodologies that have been tested to improve the performances of hybrid polymer/MOF ISG membranes. These methodologies include alteration of the physical and chemical nature of the polymer support membranes and changing the parameters of MOF growth within the membranes. While Chapter 6 describes a methodology to fabricate thin MOF films at the surface of polymer membranes to improve the permeances of hybrid polymer/MOF membranes.

Chapter 7 describes the design and fabrication of hybrid polymer/MOF membranes, both MMM and ISG, composed of iron based MOFs and polyimide P84 ISA membranes. These membranes are also tested in OSN conditions, and their structures explored and related to the fabrication methodologies employed.

This thesis is a glimpse at the possibilities available for the design and fabrication of hybrid polymer/MOF membranes. By exploring the structural and chemical properties of the hybrid polymer/MOF membranes the performances of these membranes were incrementally improved.
Chapter 2

2. Literature Review: Hybrid Polymer/Metal Organic Framework (MOF) Membranes for Organic Solvent Nanofiltration

Organic solvent nanofiltration (OSN) is a pressure driven process which utilises membranes to separate solutions on a molecular level based on size, shape and/or chemical potential. OSN membranes are typically fabricated from polymeric materials. The most common membranes used for OSN applications are integrally skinned asymmetric membranes formed via phase inversion. Polymeric membranes are cheap and flexible while the phase inversion process is simplistic and can be carried out on a large scale. However control of the phase inversion process is imprecise and molecular control of the separation layer of OSN membranes is difficult to achieve.

Therefore it is suggested that hybrid polymer/metal organic framework membranes could be designed that have the strength and flexibility of polymeric membranes, while incorporating a structured porous material into the membrane. Hybrid polymer/MOF membranes have the potential to improve solute retentions, increase membrane permeances, and reduce the effects of flux decline and membrane physical aging.

2.1 Chapter Aims

This chapter aims to discuss current hybrid polymer/metal organic framework (MOF) membranes and their applications, as well as the scope for producing new hybrid membrane technologies and expanding their applications. Existing membrane technology will be discussed and assessed and any improvements to these technologies will be suggested. The phenomena that govern transport of molecules through membranes will also be discussed and related to the design of hybrid polymer/MOF membranes. Ultimately this literature review will aid in the design of novel hybrid polymer/MOF membranes.

2.2 A Brief History of Membrane Separation Technology

Research into membrane technology is a fairly new phenomenon. Pressure driven membrane processes only began to materialize in the late 19th century, and leading journals Desalination and The Journal of Membrane Science only appeared in 1965 and 1976 respectively[9].

In the post war period the US began exploring reverse osmosis as a way of supplying water to semi-arid California. During the 1950s two researchers C.E. Reid and E.J. Breton of Florida University had begun using polymeric membranes based on cellulose for desalination[10]. In these studies several membrane types were trialled with varying, though mostly limited, success. At the same time unsuccessful trials were taking place at UCLA[9]. By the late 1950s asymmetric membranes cast from dope solutions had been made, and shown to perform well[11]. This led to the first commercial membrane desalination plant in Coalinga. The plant ran for 16 months on trial, in which time the membrane durability and reliability was tested[12]. Reverse osmosis is now an established and widely used methodology for water desalination.

Membranes have been employed for gas separations industrially since the 1980s[13], used to separate hydrogen from purge streams in ammonia production. By 2002 the market for gas separation membranes had grown to a $150 million per year[14].
Though there have been mentions in literature of OSN technology since the late 1960s[15] and 70s[16, 17], the technology has only really taken off in the 21\textsuperscript{st} century. Commercial membranes specifically made for OSN applications first became available in the late nineties from KOCH Membrane Systems[2]. Since this time a number of other companies have entered the OSN membrane market, including Evonik MET and SolSep[2].

2.3 Membrane Applications

Molecular separation applications using membranes broadly fall into three categories, desalination, gas separations and organic solvent nanofiltration (OSN). The phenomena that govern these processes and the membranes used all differ, and therefore the application of hybrid membranes in gas separations may not be applicable for OSN. Other membrane application processes exist such as microfiltration, ultrafiltration and pervaporation; however the phenomena that describe these processes can broadly be described using the same desalination, gas separation and OSN. The following section will discuss desalination, gas separation and OSN applications and the of role hybrid membranes within each.

2.3.1 A Brief Overview of Desalination

Desalination is the most widely studied and most established industrial membrane separation process. Reverse osmosis (RO) desalination processes are one of the most common ways to produce fresh water from seawater or brackish water sources[18]. The first membranes used for desalination purposes were cellulose acetate membranes[10]. These membranes were fabricated via phase inversion[19], forming an integrally skinned asymmetric membrane[20]. Current state of the art RO technology uses thin film composite (TFC) membranes composed of polyamide selective layers on top of porous polymer supports[21-24]. In recent years hybrid polymer/inorganic membranes have been developed to improve permeation, selectivity and fouling. Hybrid membranes include mixed matrix membranes composed of zeolite particles in TFC membranes[25], and carbon nanotube/polymer TFC hybrid membranes[26].

2.3.2 A Brief Overview of Gas Separation

Gas separation membranes are primarily made of polymers which fall broadly into two categories, glassy and rubbery polymers[13]. Rubbery polymeric membranes have glass transition temperatures, $T_g$, below ambient temperature, while glassy polymeric membranes have $T_g$ values above ambient temperatures[27]. PDMS is one of the most commonly used rubbery polymers used for gas separations, while common glassy polymers include polyimide and cellulose acetate[13]. Transport through gas separation membranes is governed by solution diffusion, through dense polymer membranes, or convective flow, Knudsen diffusion or molecular sieving through porous materials[28]. Polymers remain the most prolifically applied materials to produce gas separation membranes from as they can be cheaply processed to produce membranes of high surface areas in the form of hollow fibres[29]. However polymeric membrane performance is limited due to the compromise between selectivity and permeability found when using the membranes for gas separations.
Surpassing the Robeson Upper Bound

In the early 1990s Robeson showed that an upper performance limit exists for polymeric membranes, and that permeability could not be improved without compromising selectivity and vice versa[30]. Since this time the aim of those developing polymeric gas separation membranes has been to produce membranes above the Robeson upper bound. Robeson revisited the upper bound after nearly two decades and showed that only small improvements had been achieved for most separations[31].

Rubbery membranes usually have high permeabilities[27, 32] and low selectivities, whereas glassy membranes have higher selectivities but low permeabilities. Rubbery polymers include poly(organosiloxanes), such as PDMS[27]. Glassy polymers for gas separation membranes include polyimides[32, 33], especially those based on 6FDA, polycarbonates[32] polysulfones[32] and cellulose acetate[13].

Due to their limitations in selectivity and/or permeability the performances of polymeric membranes are inadequate for many industrial gas separation applications. There have been many methods developed to improve polymer gas separation membranes and overcome the Robeson upper bound, including composite polymer membranes [34, 35] and gas phase fluorination[36].

Inorganic membranes have also been developed for gas separation processes[28]. The earliest inorganic membranes were made from homogeneous porous glass, with pores between 20 and 40 Å[28]. Inorganic membranes currently developed for use in gas separation application include ceramics[37-39], zeolites[40-42] and MOFs[43, 44].

Hybrid organic/inorganic membranes known as mixed matrix membranes (MMMs) have also been used for gas separations, to improve membrane performances, while retaining some of the advantages of polymer membranes[13]. Typically MMMs for gas separation consist of an inorganic phase such as MOFs[45-50], carbon nanotubes[51] and zeolites[51-53] dispersed in a dense glassy polymer film[51].

Other forms of hybrid polymer/inorganic membrane have been produced for gas separations which utilise the growth of metal organic frameworks within polymer membranes. In-situ growth of MOFs within porous polysulfone membranes has been used to create flexible hybrid polymer/MOF membranes[54]. Thin films of MOF have also been grown in hollow fibre membranes and used to separate mixtures of H₂/C₃H₈ and C₃H₆/C₃H₈[55].

2.3.3 Organic Solvent Nanofiltration

Organic solvent nanofiltration (OSN) is a pressure driven separation process which follows the same separation principles as aqueous reverse osmosis processes. Nanofiltration processes are defined as membrane separation applications that require applied pressures between 5 and 20 bar[56]. Nanofiltration processes can also be assessed by the size of the solutes retained. Membrane processes that retain molecules lower than 2 nm in diameter are also defined as nanofiltration[57]. Based on these sizes OSN membranes typically have high retentions of solutes in the 200-1000 g mol⁻¹ molecular weight range[2].
Organic solvents are used extensively in the pharmaceutical[58] and petrochemical industries[59, 60] and also in the food industry[61]. Typical solvents include non-polar solvents such as toluene[58] and hexane[58], alcohols such as ethanol[61] and polar aprotic solvents such as N,N-Dimethylformamide (DMF)[58]. An important aspect of OSN membrane design is to find materials which are stable in organic solvent conditions with high solvent flux and the desired solute retentions[2]. A wide range of membranes have been developed to accommodate a variety of conditions[2]. Various processes have been developed to manufacture membranes leading to a range of membranes with different properties.

The most common membranes used for OSN applications are integrally skinned asymmetric (ISA) polymer membranes. Polymeric materials tend to degrade or swell in organic solvents. To produce a solvent resistant membrane the polymer usually consists of a polymeric backbone, is free of reactive groups such as –OH, and contains strong chemical bonds[62]. A number of polymeric materials have been used to create OSN membranes, including polyimide[3, 63-66], polyamide[67], and others polymers[2, 68], both in ISA and thin film composite (TFC) form. While integrally skinned asymmetric polymer membranes remain the most commonly used membranes for OSN processes, thin film composite membranes have been developed in order to improve process throughputs. Polyamide thin films have been developed for both hydrophilic[67] and hydrophobic[69] OSN processes. Hybrid polymer/inorganic mixed matrix membranes have also been developed for use in OSN processes[70, 71].

Compared to desalination and gas separation, the use of OSN membranes in commercial industrial processes is underutilised. Polymeric (polyimide) OSN membranes were successfully applied to the MAX-DEWAX process to recover solvents used in lubricant refining[72, 73]. Many OSN processes have been demonstrated at pilot-plant scale or lab scale. Applications include catalyst recovery[74-78], purification of active pharmaceutical ingredients (APIs)[79-82] and solvent exchange[83, 84].

**OSN Membrane Performance**

OSN membranes are commonly characterised by their molecular weight cut-off (MWCO) and flux[85-88], these properties are measurements of the membranes functional performance. The MWCO and flux can be measured experimentally, though results are dependent on the solvent and solutes selected.

Membrane flux is a measurement of the rate of solvent flow through the membrane, which can be calculated using **Equation 1**. Flux is measured in litres of material per hour per square metre of membrane, L m$^{-2}$ h$^{-1}$. Flux can be predicted using transport models[89]. Two prominent transport models exist, the pore-flow model and the solution diffusion model.

$$ \text{Flux} = J_v = \frac{V}{At} = \left[ L.m^{-2}.h^{-1} \right] $$  \hspace{1cm} (Equation 1)

Membrane permeance is a measure of solvent flow through a membrane independent of the applied membrane pressure. The membrane permeance can be calculated using **Equation 2**.

$$ \text{Permeance} = \frac{J_v}{\Delta P} = \frac{V}{\Delta PAt} = \left[ L.m^{-2}.h^{-1}.bar^{-1} \right] $$  \hspace{1cm} (Equation 2)
MWCO is defined as the molecular weight of a compound with a predicted 90% rejection by the membrane. Membrane rejection is a measurement of the selectivity a membrane has for a particular compound. The rejection of a solute can be found measuring the concentration of the compound in permeate and retentate and using Equation 3[85].

\[
\text{Rejection} = R_j = \left(1 - \frac{C_p}{C_R}\right) \cdot 100 = [\%] \tag{Equation 3}
\]

Most membranes selectively reject solutes based on size, retaining the larger molecules while allowing smaller molecules to pass through. Molecular weight is used as an approximation for size, though chemical structure and shape are likely to affect the actual molecular radius.

Membranes with high fluxes usually have low rejections[63]. Membrane design is often a trade-off between rejections and fluxes. Flux tends to decrease with increasing solute concentration due to osmotic pressure differences and at high concentrations concentration polarisation can occur[90, 91].

2.4 Membrane Materials and Fabrication Methodologies

This section will discuss the current methodologies and materials used to create membranes for separation purposes. While membranes for aqueous applications and gas separations will be discussed briefly, the focus will be on membranes which are used for, or may be applicable to, OSN applications. Where relevant the fabrication methodologies discussed will be related to the membrane performance, and how the parameters of the fabrication methodologies can be altered to improve those performances.

2.4.1 Polymeric Membranes

Polymeric membranes are favoured for separation processes, as they are cheap, robust and can be manufactured on a large scale. Polymeric membranes are used extensively for ultrafiltration[92, 93], organic solvent nanofiltration (OSN)[2, 63, 94], pervaporation[94], reverse osmosis[9] and gas separation[29, 95, 96]. Polymeric membranes generally fall into three categories integrally skinned asymmetric membranes, dense membranes and thin film composite membranes.

Polymer membranes are typically formed from dope solutions. To form a dope solution the desired polymer is dissolved in an appropriate solvent and/or co-solvent. For membranes formed via immersion precipitation the dope solution solvent must be immiscible in a poor solvent for the polymer. Alternatively volatile solvents could be used for evaporative phase inversion processes. Typical dope solution solvents include DMF[2, 3, 63], NMP[2, 64, 65] and DMSO[2]. The addition of co-solvents is common, and can be used to alter the properties of the finished membrane. Dioxane has been used as a co-solvent alongside DMF at varying ratios in order to change the molecular weight cut-off of polyimide membranes[3].

Dense Membranes

Dense polymeric membranes are commonly used for gas separation processes[97, 98]. Dense membranes are non-porous films in which the molecular transport is governed by solution diffusion[99]. Dense polymeric membranes are commonly formed via evaporative phase inversion
processes, leading to the formation thick dense homogenous membranes[99]. Dense polymeric membranes are typically formed by casting a dope solution on a flat surface and annealing the solution to produce a homogenous film. Permeances through dense polymeric membranes are typically slow due to their thick, non-porous nature, and therefore asymmetric membranes may be preferred for gas separation processes that require high throughput [97]. The thicknesses of these films also make them unsuitable for OSN applications.

One methodology to improve the permeance of a polymer film is to make the film thinner. Spin coating can produce homogenous polymer films less than 200 nm thick[100]. The thickness of spin coated films is a function of the density and viscosity of the polymer solution, along with the rotational speed of the solution. A dilute polymer solution, at a high spinning rate will spread to a given thickness, and once the film is thin enough the solvent will evaporate leaving a polymer film.

Ultrathin films of a polymer with intrinsic micro-porosity known as PIM-1 were produced using spin coating to achieve films as thin as 35 nm[101]. These membranes demonstrated extremely rapid rates of flux for hexane, while achieving 90% rejections of solute hexaphenylbenzene (HPB, MW = 535 g mol$^{-1}$).

Ultrathin films may not have sufficient mechanical strength to withstand high pressure OSN processes, therefore thin films are often supported by porous support membranes, and these membranes are known as thin film composite membranes.

**Thin Film Composite Membranes**

Thin film composite (TFC) membranes consist of a separate thin selective layer on top of a porous support layer made from a different material[102]. TFC membranes have higher fluxes as compared to integrally-skinned asymmetric membranes due to their ultrathin selective layers, and the highly porous support layers which offer little resistance to solvent flux. One of the main advantages of thin film composites over integrally skinned asymmetric membranes is that each layer can be separately optimised for its purpose[102]. The top layer thickness can be controlled while support layer porosity can be optimised to maximise flux. TFC membranes are extensively used in desalination because of their high permeance values and solute retentions [21-24, 103, 104]. TFC membranes have also been fabricated for OSN applications [67, 69, 105-108].

TFC membranes can be fabricated in a number of ways including, casting of ultrathin, dense films, which are then attached to porous films[102], often by techniques such as floatation deposition[101], dip coating and direct casting of a dilute solution film. However the most common TFC membrane fabrication methodology utilises interfacial synthesis, a process which was first described in the early 1980s by Cadotte et al.[109, 110].

**Integrally Skinned Asymmetric (ISA) Membranes**

The advantages of integrally skinned asymmetric polymer membranes include their flexibility, durability and ease of production. The simplified production leads to low manufacturing costs[2]. Integrally skinned asymmetric polymer membranes are designed to be flexible so they can be used within membrane modules e.g. spiral wound membrane modules[2]. Integrally skinned asymmetric (ISA) polymeric membranes contain a thin dense selective separation layer on top of a more open support layer of the same material. These membranes were first developed for aqueous
applications[11]. The most common preparation methodology for producing ISA polymer membranes is phase inversion via immersion precipitation[2].

Phase inversion is economical and reproducible, making it appropriate for commercial membrane production. The process of phase inversion turns a liquid polymer solution, known as a dope solution, into a porous solid via a process of liquid-liquid demixing. The most common method of phase inversion is immersion precipitation, in which a dope solution is submerged in a poor solvent for the polymer[2].

The composition of a polymer dope solution will contain little or no non-solvent, placing the dope solution in the area outside of the binodal region. Once the dope solution is submerged in a non-solvent, typically water, the composition of the membrane will typically follow path A, as seen in Figure 1. As the composition moves into the thermodynamically meta-stable region between the binodal and spinodal the dope solution will phase separate into a polymer rich (A') and polymer lean (A'') phase. This is the most common route for phase separation in immersion precipitation, and is known as binodal demixing. Binodal demixing progresses via a process known as nucleation and growth, whereby the polymer lean and poly rich phases will start off as a number of independent nuclei throughout the dope solution. These nuclei eventually grow as more non-solvent enters the dope solution, until the nuclei coalesce to continuous phases. A less common route to producing membranes occurs when the composition of the dope solution immediately enters the thermodynamically unstable spinodal region. This spinodal demixing also results in phase separation whereby the membrane instantly separates into two continuous, polymer rich and polymer lean phases.

The structure of ISA membranes consists of a dense selective layer on top of a more porous support layer. The surfaces of the membranes are exposed to the non-solvent first, and thus precipitate

![Figure 1: Polymer/solvent/non-solvent phase diagram demonstrating the pathways of phase separation (Adapted from ref[2]).](image)
first, the rate of precipitation for the layers below the dense separation layer are slower, as the rate 
of composition change in the membrane slows\cite{111, 112}.

The structure of polymer membranes formed via immersion precipitation can also be influenced 
but the kinetics of the demixing process. Delayed demixing and instantaneous demixing can lead to 
 vastly different membrane structures. Figure 2 shows the composition of a membrane at the top 
(1), middle (2) and bottom of the membrane (3) at time = t, a point very soon after the membrane 
dope solution has been submerged, i.e. less than 1 sec. In instantaneous demixing at time t the non-
solvent has reached the interior of the membrane already, and phase separation has already begun. 
For delayed demixing processes at time t all regions of the membrane are in the stable phase region, 
and demixing will only occur once the non-solvent has entered the membrane interior.

![Figure 2: Polymer/solvent/non-solvent phase diagram demonstrating membrane composition at 
time < 1 sec at different points of the membrane for (left) instantaneous demixing and (right) 
delayed demixing (adapted from ref\cite{2})](image)

Control of the demixing process allows for some degree of control of the properties of the final 
membrane. As far back as 1975 the rejection and flux behave of cellulose acetate membranes were 
controlled by altering the precipitation rate of the dope solution\cite{111}. Membranes with slow 
precipitation rates produced membranes with sponge-like support structures and high salt 
rejections, while membranes with fast precipitation rates produced membranes with large 
macrovoids and lower salt rejections. Systems with high heats of mixing and rapid membrane 
precipitations produce membranes with finger like structures, whereas systems with low heats of 
mixing and slow precipitation produce membranes with sponge like structures\cite{112}.

The production of macrovoids is associated with low mechanical strength and membrane 
compaction\cite{2}. Therefore it has sometimes been desirable to produce membranes without finger 
like structures, while still maintaining high fluxes. As has been shown earlier, solvent/non-solvent 
selection can have a profound effect on the kinetics of the phase inversion process. The phase 
inversion process can also be influenced by the position of the binodal and spinodal lines in the 
phase diagram\cite{113}. The Polyimide (PI)/DMSO/water system has an extremely narrow miscibility 
region, as compared to a more typical PI/NMP/water system. The narrowness of the miscibility gap 
is likely due to the high solubility of DMSO in water, alongside the extremely low solubility of PI in 
water. The narrowness of the miscibility gap, the closeness of the binodal and spinodal lines and the

\[\]
subsequent positions of the gelation point in the phase diagram means that the phase separation process finishes at an early stage, restricting the growth of the polymer lean phase. This means the phase separation process is ‘frozen’ before the formation of macrovoids can occur.

As well as controlling the structural properties of OSN membranes, the performances of OSN membranes have been controlled via alteration of the dope solution mixture[3]. The addition of a volatile co-solvent in the dope solution mixture was shown to increase solute retentions, with increasing co-solvent content[3, 114, 115]. Addition of co-solvent changes the phase inversion behaviour from instantaneous demixing to delayed demixing. Delayed demixing had previously been shown to reduce the formation of macrovoids and produce tighter membranes[111]. The work by See-Toh et al. also states that the volatility of co-solvent (in this case dioxane) may cause the surface of the membrane to become polymer rich prior to immersion precipitation, via solvent evaporation. This may contribute to increased solute retentions. The properties of polyimide membranes, such as flux, have also been controlled by altering parameters such as membrane casting thickness and annealing time[116].

Table 1: List of polymers used to produce OSN membranes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Membrane Type</th>
<th>Solvents Tested to be Stable in:</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyimide P84</td>
<td>ISA</td>
<td>Methanol, Ethanol, Toluene, Ethyl acetate, Heptane</td>
<td>[89, 117]</td>
</tr>
<tr>
<td>Crosslinked Polyimide P84</td>
<td>ISA, TFC support membranes</td>
<td>As above plus: DMF, NMP, DMSO, DMAC, Acetone</td>
<td>[63, 67, 69]</td>
</tr>
<tr>
<td>Polyimide Matrimid</td>
<td>ISA</td>
<td>Heptane</td>
<td>[101]</td>
</tr>
<tr>
<td>Polyamide (on polyimide supports)</td>
<td>TFC</td>
<td>Methanol, DMF, Acetone, Ethyl acetate, Toluene, THF</td>
<td>[67, 69]</td>
</tr>
<tr>
<td>Crosslinked Polybenzimidazole (PBI)</td>
<td>ISA</td>
<td>Acetonitrile, DMF, methanol, additional stability in acid and basic conditions</td>
<td>[79, 118]</td>
</tr>
<tr>
<td>Polyether ether ketone (PEEK)</td>
<td>ISA</td>
<td>DMF, Isopropyl alcohol, THF additional high temperature stability</td>
<td>[74, 119]</td>
</tr>
<tr>
<td>Polydimethylsiloxane (PDMS) (on PAN supports)</td>
<td>TFC</td>
<td>Acetone, THF, Heptane, Ethanol, Methanol, Ethyl Acetate, Toluene, Isopropyl alcohol, Hexane, Octane, Cyclohexane, Xylene</td>
<td>[120, 121]</td>
</tr>
<tr>
<td>Polyacrylonitrile (PAN)</td>
<td>TFC support membranes</td>
<td>Acetone, THF, Heptane, Ethanol, Methanol, Ethyl Acetate, Toluene, Isopropyl alcohol, Hexane, Octane, Cyclohexane, Xylene</td>
<td>[101, 120, 121]</td>
</tr>
<tr>
<td>PIM-1</td>
<td>Dense, TFC</td>
<td>Heptane, Toluene, Acetone, Chloroform, THF</td>
<td>[101, 117]</td>
</tr>
</tbody>
</table>
Despite the options available to alter the phase inversion process, the process cannot produce membranes with precise regular pore sizes. Calculations by See-Toh et al. show that the despite changing the MWCO, each membrane still has a pore size distribution, rather than a single controllable pore size[3]. The pore size distributions of OSN membranes with different MWCOs were explored physically by Stawikowska and Livingston[122]. Using osmium dioxide nanoparticles the pore size distribution of OSN membranes with different MWCOs formed using varied solvent/co-solvent ratios showed that despite the alterations, each membrane had a pore size distribution of varying range. These pore size distributions ranged from 0.5 to 1.1 nm, 0.7 to 1.7 nm and 0.6 to 1.8 for MWCOs of 300 g mol$^{-1}$, 1200 g mol$^{-1}$ and 1400 g mol$^{-1}$ respectively. When the pore flow transport model was applied to the membranes, it was shown that, membranes with uniform pore sizes, rather than the distributions present, display improved solute retention performances[123].

It is the lack of control in the phase inversion process which has led to increased interest in producing membranes with more molecular design in the selective layer of the membrane. One possible way to achieve this is through the use of inorganic and/or crystalline membranes with uniform, predictable pore sizes.

### 2.4.2 Inorganic and Crystalline Membranes

For comparable selectivities inorganic membranes can have permeances up to ten times higher than polymeric membranes[124]. The porous structure of some inorganic/crystalline materials can be controlled to produce membranes with regular, repeatable porous structures with a single defined pore size, such as those found in zeolites and metal organic frameworks. However inorganic membranes tend to be brittle and unsuitable for use in membranes modules. The main categories of inorganic/crystalline separation membranes are ceramic membranes, zeolite membranes and metal organic framework membranes.

Ceramic membranes are fabricated from metal oxides such as aluminium oxide (aka alumina) and zirconium oxide (zirconia)[125]. Ceramic membranes have been used for gas separation, pervaporation and OSN separations. Porous ceramic membranes have an asymmetric structure with several layers of material, with decreasing porosity laid on top of one another[2]. The active layers of ceramic membranes are made via sol-gel synthesis; the pore size distribution of ceramic membranes can be controlled by altering the sizes of particle in the sol-gel. Ceramic membranes can be formed in hollow fibres via spinning/sintering processes[126, 127]; this means ceramic membranes can be used in high surface area to volume modules.

Common routes for producing zeolite membranes include hydrothermal synthesis and dry-gel conversion[128]. Zeolite membranes have been applied to the separation of organic compounds from aqueous solution, gas separations and separations of chiral molecules[129]. Zeolite membranes have been grown on alumina and titania porous supports[129, 130]. Seeding has been used to direct the growth of zeolite crystals onto porous supports, after which hydrothermal synthesis is conducted to produce the zeolite film. Many of the methodologies used to produce zeolite membranes have been applied to form MOF membranes.

HKUST-1 is one of the most common MOFs used to fabricate inorganic membrane films[131-133]. Using standard solvothermal methodologies, a dense layer of HKUST-1 was grown on the surface of an asymmetric disk of α-alumina[131]. Using crystal seeding techniques via a layer by layer
fabrication methodology, HKUST-1 was grown on a porous alumina support, and tested for the separation of hydrogen in several gas mixtures[132]. Using a seeded porous alumina support MIL-53 was grown in a dense layer using solvothermal synthesis[134]. The membrane was used to separate ethyl acetate and water.

2.4.3 Hybrid Polymer/Inorganic Membranes

Hybrid membranes offer the opportunity to incorporate the selective nature of inorganic/crystalline materials, with the flexibility and durability of polymer membranes. Most hybrid membranes fall into a category known as mixed matrix membranes (MMMs). Many of the materials used to create polymer membranes and inorganic membranes can be used to create mixed matrix membranes. Typically mixed matrix membranes consist of a continuous polymer phase in which discrete inorganic/crystalline materials are dispersed[13, 135]. MMMs are designed to utilise the best separation properties of both polymer and inorganic materials, as a methodology to overcome the Robeson upper bound for gas separations.

Originally MMMs filled with zeolites, were designed for gas separation processes[13, 136-140] and organic solvent separation via pervaporation[141]. Zeolites, molecular sieves, have been added to polymer membranes to improve selectivities[142, 143]. Interactions between the inorganic filler particles and the polymer are very important to the fabrication of MMMs. It was found that while interactions between zeolites and rubbery polymers allowed for good adhesion, MMMs composed of zeolites and glassy polymers such as polyimide allowed for the formation of non-selective voids[144]. However adhesion between the inorganic and polymer phases of MMMs has been improved through the use of chemical agents to improve compatibility between the phases[145]. Chemical agents have also been used to alter zeolite particles to improve the interaction between the polymer and zeolite phases[146]. Silanation is a way to alter the chemical nature of the surfaces of zeolite particles and introduce functional groups to the zeolite surface which can react with the polymer. Other methodologies employed to improve adhesion between zeolites and polymers include annealing of the membrane, the addition of low molecular weight materials and adaptation of the polymer itself[52].

The adhesion of the inorganic and polymer phases is also dependant on the parameters of MMM fabrication. Typical MMM fabrication is very similar to polymer membrane fabrication. First a dope solution is formed which contains the desired inorganic filler particles[51]. The dispersion of particles in MMM dope solutions is usually designed to reduce the effects of particle agglomeration. One methodology to improve the adhesion between filler particles and polymer in the dope solution is through priming[52]. The inorganic particles are initially mixed with a small percentage of the polymer, to discourage agglomeration between the particles. The rest of the polymer is added to the dope solution once inorganic particles are sufficiently mixed.

The membranes are then fabricated via phase inversion. For dense gas separation membranes evaporative methodologies are employed, and for asymmetric membranes immersion precipitation is used. The addition of inorganic particles in membrane dope solutions can influence the parameters of the phase inversion process for MMMs. Non-porous filler particles can also be added to MMMs to alter the morphology of the polymer in the membrane, which can lead to improved separations and permeabilities[51]. Inorganic particles have been added to polymer membranes in order to alter the morphology of the membrane so as to improve permeance performances.
Titanium dioxide has been added to integrally skinned asymmetric polymer membranes to produce MMMs used to combat flux decline in OSN[147]. The addition of TiO₂ particles to polyimide dope solutions was shown to suppress macrovoid formation in the membranes.

Transport through MMMs can be modelled using the Maxwell model[139, 148-152] or other models such as the Bruggeman model[150, 151]. As MMMs contain discrete particles of inorganic filler in a continuous polymer network, the permeation flow path through these membranes is modelled as a composite of the permeability characteristics of the inorganic material and the polymer. This means that there is a limit to the influence the inorganic filler can have on the permeation properties of MMMs. The interaction between the polymer and the MOF is very important to the transport properties of MMMs. The Maxwell model assumes perfect interaction between the MOF and the polymer, however the formation of non-selective voids, rigid polymer layers and polymer incursion into the MOF can reduce the effectiveness of MMMs[70, 139, 153-155].

Metal-organic frameworks have been suggested for gas separation processes due to their porous structure, and adsorption properties[44, 45, 47-49, 139, 156, 157]. They have also been suggested for organic solvent nanofiltration processes[70, 158].

As with zeolite particles MOF based MMMs were originally designed for gas separation purposes. MOF based MMMs are said to have a number of advantages over other choices of inorganic filler. Firstly the presence of organic linkers in MOFs makes compatibility between the particles and the polymer phase stronger[159]. This reduces the formation of non-selective voids. The pore size and chemical functionalities of MOFs can also be readily controlled for separation or catalytic processes[159-162]. The adaptability of MOF metal ions and organic linkers has led to the formation of thousands of MOF structures.

Many different MOFs have been incorporated into the structures of dense polymeric membranes, thin film composite membranes and integrally skinned asymmetric membranes for gas separation, OSN and pervaporation applications. A list of some of the MOFs that have been used in MMMs can be found in Table 2.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Polymers Used With:</th>
<th>Membrane Type</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>Matrimid, PDMS, PSf, P84</td>
<td>Dense membrane, TFC</td>
<td>Gas Separation, OSN, Pervaporation</td>
<td>[45, 70, 163-165]</td>
</tr>
<tr>
<td>MIL-47</td>
<td>PDMS</td>
<td>TFC</td>
<td>OSN</td>
<td>[70]</td>
</tr>
<tr>
<td>MIL-53</td>
<td>PDMS, Matrimid, P84, Polyamide</td>
<td>Dense membrane, TFC, ISA</td>
<td>Gas Separation, OSN</td>
<td>[70, 158, 163, 164]</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>PDMS, Matrimid, Polyamide, 6FDA-durene</td>
<td>Dense membrane, TFC, ISA</td>
<td>Gas Separation, OSN, Pervaporation</td>
<td>[47, 70, 158, 163, 166, 167]</td>
</tr>
<tr>
<td>MOF-5</td>
<td>Matrimid</td>
<td>Dense membrane</td>
<td>Gas Separation</td>
<td>[48]</td>
</tr>
<tr>
<td>Mn(HCOO)₂</td>
<td>Psf</td>
<td>Dense membrane</td>
<td>Gas Separation</td>
<td>[45]</td>
</tr>
<tr>
<td>Fe-BTC</td>
<td>P84</td>
<td>Dense membrane</td>
<td>Gas Separation</td>
<td>[164]</td>
</tr>
<tr>
<td>MIL-101(Cr)</td>
<td>Polyamide</td>
<td>TFC</td>
<td>OSN</td>
<td>[158]</td>
</tr>
<tr>
<td>ZIF-7</td>
<td>Chitosan</td>
<td>Dense membrane</td>
<td>Pervaporation</td>
<td>[168]</td>
</tr>
</tbody>
</table>
Despite the improved adhesion between polymers and MOFs the formation of non-selective voids still occurs. Non-selective voids have been reduced in MOF based MMMs through use of priming[163], sealing membranes with silicone[156, 163], chemical modification of the MOF particles[70, 166, 169, 170] and crosslinking of the MMM[166]. Amines are commonly used to improve adhesion between polymers and MOFs, and have also been used to crosslink polyimide membranes, to improve the solvent stability of the membranes[63, 64].

MMMs containing MOFs have been produced for applications in OSN; where their porous nature utilised is to improve the performance of thin film composite membranes[70, 158]. Rejections of over 90% for Rose Bengal in isopropyl alcohol have been achieved using MMMs, prepared using HKUST-1 or MIL-47 crystals. The MOF crystals were dispersed in PDMS/Hexane solutions, which were then cast on top of polyimide ISA membranes to create TFCs. Initially the MMMs performed poorly compared to the unaltered PDMS membranes, due to poor adhesion between the polymer and the MOFs, allowing for the formation of non-selective voids in the membrane. Using N-methyl-N-(trimethylsilyl)-trifluoroacetamide (MSTFA) to modify the MOFs, adhesion to the polymer was improved, increasing the rejection of Rose Bengal. This work shows that for liquid applications, the performance of MMMs is highly influenced by the formation of non-selective voids. A large increase in membrane flux was observed for the unmodified MMMs, which was attributed to the presence of the non-selective voids. The MMMs containing modified MOFs displayed improved retentions, while the permeances were similar to the pure PDMS membranes. This indicates that for this application the MOF was used to act as a molecular sieve, encouraging the retention of the solute molecular, while allowing the solvent to flow through the membrane.

MOF particles have been incorporated into the selective layer of polyamide TFC MMMs created via interfacial synthesis[158]. MOFs were first dispersed in a trimesoyl chloride (TMC) solutions in hexane, which was reacted with an aqueous m-Phenylenediamine (MPD) solution orientated at the surface of a polyimide support membrane. This resulted in the formation of a thin polyamide film containing interspersed MOFs. The addition of MOF nanoparticles was shown to increase the permeance of TFC membranes, with highly porous MIL-101(Cr) leading to the largest increase in membrane flux. For these TFCs, unlike those fabricated by Basu et al., solute retentions were not improved, as the cage size of MIL-101(Cr) is significantly larger than the size of the solutes being filtered. It can be theorised that the MOFs offer no selective capabilities in these membranes. The advantage of adding MOFs to TFC membranes fabricated via interfacial synthesis is to introduce porous channels into the membrane which improve permeability. MIL-101(Cr) is hydrophobic in nature, and was shown to increase the permeance of THF, the more hydrophobic solvent, to a greater degree than, hydrophilic, methanol.

Despite advances in MMM fabrication, issues of non-selective void formation and the discrete nature of the filler materials in MMMs means that the transport properties of these hybrid membranes are not completely controlled by the inorganic material. To alleviate these issues, an alternative methodology, in which inorganic/crystalline material is grown in the pores of pre-existing polymer membranes, has been employed. MOF films have been grown directly onto polymer surfaces, demonstrating the ability for polymers to act as supports for MOF based membranes[171, 172]. In-situ growth (ISG) of MOF material has been used to create flexible hybrid polymer/MOF
membranes for gas separations[54, 173]. HKUST-1/PSf and ZIF-8/PSf hybrid polymer/MOF membranes were fabricated via layer by layer deposition of reagents with drying between deposition steps[54]. The presence of the MOF in the membranes was confirmed using X-ray powder diffraction. The membranes displayed improved selectivities for both H₂/C₃H₆ and H₂/CO₂, although gas permeances were decreased. Hybrid ZIF-8/PSf membranes formed by ISG were shown to outperform other ZIF-8/polymer hybrid membranes with regards to selectivity[173].

Hybrid membranes formed via in-situ growth of MOFs in polymer films have been shown to have high selectivities; however the permeances through these membranes are low. Improving permeances could be achieved by growing thin films of MOF. ZIF-8 thin films have been grown on the surface of polymer hollow fibre membranes and used for gas separation applications[55]. The ZIF-8 film is formed via interfacial synthesis; the reactants are orientated to meet at the surface of the polymer hollow fibre membranes, producing a thin film, which is self-completing. HKUST-1 has been shown to be able to be produced via interfacial synthesis, showing that this methodology could be extended to other MOFs[174].

In-situ growth of inorganic material has also been applied to membranes used for OSN purposes[71]. 3-Aminopropyl trimethoxysilane (APTMS) was used as a crosslinking agent in polyimide nanofiltration membranes. The APTMS molecules were shown to form an organosiloxane network throughout the membranes via a hydrolysis reaction. The subsequent inorganic network was shown to reduce the effect of compaction and flux decline in the membranes. The structural support added by the organosiloxane network also removed the need to add conditioning agent to the membranes to preserve the pores. While the membranes were shown to have high rejections, the membrane fluxes were reduced below pure polymeric based membranes.

2.5 Transport Models

The following models serve to describe how solute and solvent molecules are transported through membranes, and how the predicted transport relates to the observed separation properties of membranes. The most common transport models applied to OSN membranes are the solution diffusion model and the pore flow model. The transport through composite materials is often predicted using the Maxwell model.

2.5.1 Solution Diffusion Model

The solution diffusion model was devised by Lonsdale et al. to describe the separation of water and salt ions by cellulose acetate[175]. Lonsdale et al. also used the solution diffusion model to describe transport through membrane for the separation of organic solvent phenol from water[15]. In the solution diffusion model molecules are said to dissolve into the structure of the membrane, rather than flowing through channels present in the membrane. This makes the solution diffusion model suitable to describe transport through dense polymer or inorganic films, such as those used in gas separations. Dissolved molecules diffuse through the membrane, due to the chemical potential gradient through the membrane. Separation occurs due to differences in solubility and diffusivity of species. For the solution diffusion model, flux through the membrane can be described using Fick’s law. The equation describing solvent flux in the solution diffusion model can be found in Equation 4.
\[ J_1 = -D_1 \frac{dC_1}{dx} \]  \hspace{1cm} \text{(Equation 4)}

Where \( J_1 \) is the flux of solvent, \( D_1 \) is the diffusivity of solvent, and \( dC_1/dx \) is the concentration gradient of solvent across the width of the membrane.

The chemical potential of the solvent dissolved in the membrane, \( \mu_1 \), can be written as a function of the concentration of solvent in the membrane, this can be seen in Equation 5.

\[ \mu_1 = \text{constant} + RT \ln C_1 \] \hspace{1cm} \text{(Equation 5)}

Combining Equation 4 and Equation 5 gives the flux in terms of chemical potential across the width of the membrane. This can be seen in Equation 6.

\[ J_1 = - \frac{D_1 C_1}{RT} \frac{d\mu_1}{dx} \approx \frac{D_1 C_1}{RT} \frac{\Delta \mu_1}{\Delta x} \] \hspace{1cm} \text{(Equation 6)}

For low concentration systems the concentration difference of solvent between the feed and permeate is negligible. As OSN is a pressure driven process, the difference in chemical potential between the solvent in the feed and permeate is caused by the difference in pressure between the solutions. Therefore the chemical potential change throughout the membrane can be described in terms of the applied and osmotic pressure of the system (see Equation 7).

\[ \Delta \mu_1 = \bar{V}(\Delta P - \Delta \pi) \] \hspace{1cm} \text{(Equation 7)}

Where \( \bar{V} \) is molar volume of the solvent, \( \Delta P \) is the applied pressure difference been the feed and permeate and \( \Delta \pi \) is the osmotic pressure difference between the feed and the permeate. Combining Equation 6 and Equation 7 gives the flux of the solvent.

\[ J_1 = - \frac{D_1 C_1 \bar{V}(\Delta P - \Delta \pi)}{RT \Delta x} \] \hspace{1cm} \text{(Equation 8)}

The flux of solutes through membranes can also be described using Fick’s law of diffusion.

\[ J_2 = -D_2 \frac{dC_2}{dx} \] \hspace{1cm} \text{(Equation 9)}

Where \( J_2 \) is the flux of solvent, \( D_2 \) is the diffusivity of solute, and \( dC_2/dx \) is the concentration gradient of the solute across the width of the membrane. For the solute the change in chemical potential is largely governed by the difference in concentration between the feed and permeate solutions. Therefore the flux of the solute can be described by the concentration difference across the membrane. The concentration of the solute in the membrane is determined by the concentration of solute in the bulk outside the membrane, \( \rho \), and \( K \), a coefficient related to the extent of sorption of the solute into the membrane.

\[ J_2 = -D_2 \frac{\Delta C_2}{\Delta x} = -D_2 K \frac{\Delta \rho_2}{\Delta x} \] \hspace{1cm} \text{(Equation 10)}
The rejection of solutes can be found by calculating the ratio of solvent and solute fluxes through the membrane. This is a simplified version of the solution diffusion model which has been shown to be true for aqueous solutions and salts. Various adaptations have been devised to describe organic solvent nanofiltration separations[176].

2.5.2 Pore Flow Model

The pore flow transport model describes the diffusion of molecules through cylindrical pores. This transport model can be readily applied to materials with known pore sizes such as MOFs. Separation occurs due to molecular sieving, caused by size exclusion and steric hindrance within the pore. The driving force of flux through pores is a pressure gradient across the width of a membrane[177]. The flux through a pore can be described using the Hagen–Poiseuille model[178] (see Equation 11).

\[
J_1 = \frac{r_p^2(\Delta P - \Delta \pi)\varepsilon}{8\mu_{p,1}\Delta x} \quad \text{(Equation 11)}
\]

Where \(r_p^2\) is the radius of the pores of the membrane, \(\Delta P\) is the applied pressure difference between the feed and permeate and \(\Delta \pi\) is the osmotic pressure difference between the feed and the permeate. While \(\varepsilon\) is the porosity of the membrane, \(\mu_{p,1}\) is the viscosity in the pore, and \(\Delta x\) the thickness of the membrane selective layer.

The viscosity of solvent in the pore is higher than the bulk viscosity of the solvent, as the viscosity of the solvent at the pore wall is higher than the viscosity in the centre of the pore, due to friction between the pore wall and the solvent molecule. The ratio of the viscosity in the pore, \(\mu_{p,1}\), and the viscosity of the bulk solvent, \(\mu_0\) can be calculated using Equation 12 devised by Bowen and Welfoot[177].

\[
\frac{\mu_{p,1}}{\mu_0} = 1 + 18\left(\frac{d_1}{r_p}\right) - 9\left(\frac{d_1}{r_p}\right)^2 \quad \text{(Equation 12)}
\]

Equation 12 is derived from the assumption that the viscosity at the pore wall is 10 times that of the bulk viscosity, by averaging the viscosity of the pore wall and the centre of the pore the above equation is found. The relationship between bulk viscosity and pore viscosity was initially devised for nanofiltration membranes used in aqueous conditions, where \(d = 0.28\) nm. Organic solvent molecules are typically much larger than water molecules; therefore the ratio of pore radius to diameter of solvent molecule will be much different. It may be that the assumption does not hold up for OSN processes, however this equation goes some way to correcting for the effect of increased viscosity in the pores of membranes.

For a dilute system the flux of the solvent through the membrane is a good estimate for the overall flux through the membrane. For non-charged systems the rejection of solutes in the pore flow model can be found using Equation 13.

\[
R_j = 1 - \frac{\Phi_{pc,12}K_{c,12}}{1-(1-\Phi_{pc,12}K_{c,12})(exp(-Pe_{12}))} \quad \text{(Equation 13)}
\]
Where $\Phi_{pc,12}$ is the partition coefficient between the solvent (1) and solute (2), $K_{c,12}$ is the coefficient of convection of the solute through the solvent and $Pe_{12}$ is the Peclet number, which characterises the transport of the solute through the pore. The equations that describe these coefficients were used to calculate the rejection in porous OSN membranes by Stawikowska et al. [123].

In the pore flow model, as well as molecular sieving effects, the rejection of solutes is due to the differential flux between the solute and solvent molecules. Solvent molecules, which are smaller than solute molecules, are statistically less likely to suffer from steric hindrance interacting with pore walls. The larger a solute molecule is the more likely that the transport of the solute molecule is impeded by interactions with the pore wall. The pore-flow model can be used to model transport through a membrane with a single regular pore size, such as MOFs, and transport through membranes with a pore size range [123], such as integrally skinned asymmetric membranes.

The pore flow model is more suitable for modelling transport and separation through porous inorganic membranes such as MOFs. Therefore for hybrid polymer/MOF membranes the pore flow model may be used to predict rejection. However these will only be accurate for films without defects, and where rejection is completely controlled by the porous nature of the MOF.

### 2.5.3 Maxwell Model

The Maxwell model can be used to predict the permeability through a mixed matrix membrane. The Maxwell model was originally used to describe conductivity in composite materials [139, 179]. The Maxwell model equation (see Equation 14) can predict the effective permeability of a gas through a dilute suspension of spherical particles in a continuous phase.

$$P_{\text{eff}} = \frac{P_c [P_d + 2P_c - 2\phi(P_c-P_d)]}{P_d + 2P_c + \phi(P_c-P_d)}$$  \hspace{1cm} (Equation 14)

Where $P_{\text{eff}}$ is the effective permeability of the composite membrane, $P_c$ is the permeability of the continuous phase, $P_d$ is the permeability of the dispersed phase and $\Phi$ is the volume fraction of the dispersed phase.

The Maxwell model equation assumes that there is perfect adhesion between the polymer and inorganic phases of the membranes. The Maxwell model has been adapted to predict membrane permeability in the non-ideal cases of membranes with non-selective voids, polymer incursion into pores and polymer rigidification [139, 179]. Other models exist to predict the permeability of mixed matrix membranes, including the Bruggeman model [150, 151, 179] and the Lewis-Nielsen model [179].

### 2.6 Metal Organic Frameworks (MOFs)

Metal Organic Frameworks (MOFs) are crystalline compounds consisting of metal ion or cluster ions connected by organic ligands [4]. Over a thousand MOFs have been reported in literature, commonly cited structures include HKUST-1 (Cu-BTC) [4, 131], MOF-5 [4, 48], MIL-53 [4] and ZIF-7 [180, 181]. MOFs are of scientific interest due to their porous structures, large surface areas and versatility. MOFs have also been referred to as porous coordination polymers (PCPs) [4, 5], hybrid organic–inorganic materials [5] and organic zeolite analogues [5]. Due to their regular porous structures, MOFs have been suggested for separation processes.
MOFs are regular frameworks with consistent pore sizes and orientations, they have large surface area to volume ratios and due to the large number of inorganic-organic combinations possible the chemical properties of MOFs can be altered for specific applications. The properties of metal-organic frameworks make them suitable for a number of applications including, catalysis[4], organic solvent nanofiltration[70], gas separation[4], gas Storage [4], magnetism[4], optics[4], sensors[4] and drug delivery[4].

Metal organic frameworks can orientate themselves in a number of different ways, ranging from frameworks with pores small enough to exclude any molecular transport, known as 0D cages, or 3D interconnected porous networks. Between these two extremes lie MOFs composed of 1D channels. These channels connect together to make 3D cage networks. MOFs can also form 2D flat sheets, which can be stacked on top of each other, allowing molecules to be trapped by the MOF sheets.

MOF networks come together in a two-step process. First, secondary building units (SBUs) centred on ligands are made. These SBUs then combine to create the porous frameworks[4, 162]. Using this methodology MOF structures can allow for pore sizes much larger than the diameters of the metal ion and organic ligands used to build the MOF.

A number of fabrication methods have been developed to fabricate MOFs, which include, Solvent-Evaporation Synthesis[4], Hydrothermal (or Solvothermal) Synthesis[4], Diffusion Synthesis[4], Microwave-Reaction Synthesis[4], Ionothermal Synthesis[4], Electrochemical Synthesis[4] and High-Throughput Synthesis[4].

These methodologies have been devised to create the thermodynamic conditions required to form high purity, regular and predictable MOF structures. For solvent-evaporation synthesis a solution containing the MOF component molecules and ions is slowly saturated. Slow saturation is required to form large regular crystals with few defects. The solution is usually saturated by evaporation of the solvent at room temperature, though occasionally cooling crystallisation is employed[4].

Solvothermal synthesis requires the use of an autoclave, a high pressure reaction vessel. The autoclave is heated to a desired temperature for anything from a couple of hours to a couple of days [4, 131, 181-183]. Typical reaction temperatures are around the 100°C region. This synthesis method was developed from methodologies employed to build zeolites. Microwave-reaction synthesis is very similar to solvothermal synthesis processes except microwaves are used to energise the reaction, vastly reducing the time required to carry out the reaction[184, 185].

Diffusion synthesis slowly brings together the building blocks of the metal organic frameworks in two separate phases, one containing the organic ligand, the other containing the metal ion. The MOF crystallises in the middle phase, usually at the interface. The methodology slowly produces crystals over a period of days[186]. This interfacial synthesis methodology has been used to create MOF thin films[174].

Ionic liquids have been used as solvents for MOF fabrication processes as the ionic nature of solvent could influence the coordination of the metal ions and thus the structure of the MOF crystals[187]. Ionic liquids can also affect MOF chirality[188].

Another methodology to produce MOFs is via electrochemical synthesis[189]. MOF HKUST-1 was made using electrochemical synthesis. An electrical current of 1.3A with a voltage of 9-12V was
passed through a methanol solution containing the organic linker 1,3,5-benzenetricarboxylic acid. Bulk copper anodes and a copper cathode were used and MOF crystals were formed in a matter of hours.

Metal organic frameworks have been suggested as possible heterogeneous catalysts[160, 183, 186, 190, 191] in reactive processes. This is due their large internal surface areas, the catalytic activity of transition metal ions and the possibility to increase catalytic activity further by replacing the metal ions and organic ligands with active catalysis sites. MIL-53 and IRMOF-5 have been used to catalyse reactions, including the Knoevenagel condensation of ethyl cyanoacetate and ethyl acetoacetate with benzaldehyde[190]. On this occasion the organic linker catalysed the reaction.

**HKUST-1**

HKUST-1, one of the most widely studied and understood MOFs [4, 131], is a copper based MOF with benzene tricarboxylic acid ligands. The chemical formula for HKUST-1 is Cu$_3$(BTC)$_2$. Typically during formation HKUST-1 pores are solvated with water or DMF molecules, depending on the solvent choice for the reaction. The typical size of HKUST-1 crystals formed via solvothermal synthesis is between 10 to 20 µm[183, 192, 193], though nanoparticle size HKUST-1 crystals can be produced via ultrasonic or microwave synthesis[192, 194] or freeze drying[195]. The pore size of HKUST-1 (cage windows of 0.9 nm[196, 197]) is suitable for OSN separations. HKUST-1 has a BET surface area of around 1200 m$^2$ g$^{-1}$[198, 199].

HKUST-1 has been used as a catalyst for the cyanosilylation of benzaldehyde and acetone. The copper ions act as the catalyst in this case; yields of 57% were achieved after 72 hours, as compared to 10% yield achieved with no catalyst present[183]. HKUST-1 has been used to catalyse the oxidation of benzylic compounds with t-butyl hydroperoxide in acetonitrile[191]. The large surface areas of the MOF and the activity of the copper ions allowed yields of over 80% to be achieved. HKUST-1 and similar frameworks with some of the BTC linkers replaced with pyridine-3,5-dicarboxylate (PyDC) were used to catalyse the hydroxylation of toluene in acetonitrile[160]. It is suggested that due to the copper ions being held in place offering specific bonding sites with the reactants undesired side reactions could be avoided. This was shown by comparing reaction selectivity of the MOFs with reactions carried out with homogeneous catalysis of dissolved cooper ions. HKUST-1 has also been used to catalyse the cyclisation of citronellal[200].

**Iron Carboxylate MOFs**

Iron carboxylate MOF networks come in two main forms, MIL-100(Fe)[185, 201-204] and Fe-BTC[203]. The synthesis and structure of MIL-100(Fe) is well understood, while the structure of Fe-BTC is less well understood, however research has shown Fe-BTC to be a good catalyst. MIL-100(Fe) has a BET surface area of 2200 m$^2$ g$^{-1}$, while Fe-BTC has a BET surface area of 840 m$^2$ g$^{-1}$[203].

Iron, as a transition metal, has been used for several catalytic applications[205-208]. Therefore Iron based MOFs with high surface areas have been applied to a number of catalytic applications[201-204, 209]. Fe-BTC was used to catalyse the oxidation of benzylic compounds with t-butylhydroperoxide in acetonitrile[191]
2.7 Conclusions

While polymeric integrally skinned asymmetric membranes remain the most commonly used membranes for OSN processes, the fabrication methodology employed to create them, phase inversion via immersion precipitation, does not allow for molecular control of the membrane porous structure. The phase inversion process cannot readily be controlled, and studies show that immersion precipitation will always lead to the fabrication of membranes with a distribution of pore sizes. Inorganic materials such as zeolites, or metal organic frameworks (MOFs), can be used to create membranes for separations; however, the fabrication of these membranes is difficult to scale up and expensive. Therefore, hybrid polymer/inorganic membranes have been developed in order to produce membranes that are flexible, while also incorporating the selective properties of inorganic materials.

Two main fabrication methodologies exist to produce hybrid polymer/MOF membrane mixed matrix membrane (MMM) and in-situ growth (ISG). The discrete nature of inorganic particles in MMMs means that the performance of the membranes can never be fully controlled by the pores of the inorganic material. This is shown by the Maxwell model, in which the membrane permeance will always be determined partly by the permeability of the continuous phase. To rectify the problems associated with MMMs, a new hybrid membrane fabrication methodology has been devised for gas separation membranes, known as in-situ growth, whereby inorganic materials are grown within and on top of polymer support membranes. This hybrid membrane fabrication methodology has the potential to create flexible membranes in which the separation properties are completely controlled by the porous nature of the inorganic filler.

This thesis will explore the fabrication of hybrid polymer/MOF membranes for the OSN applications, including MMMs and in-situ growth membranes. The suitability of these membranes for OSN processes will be assessed and compared to existing polymer membranes.
Chapter 3

3. Study of Asymmetric Metal Organic Framework Mixed Matrix Membranes in OSN Applications

3.1 Introduction

The literature review in Chapter 2 shows that polymeric membranes are favoured for separation processes, as they are cheap, robust and can be manufactured on a large scale. Porous, crystalline inorganic materials e.g. ceramics, zeolites and porous carbon as well as metal organic frameworks, have also been used for separation processes. For comparable selectivities inorganic membranes can have permeabilities up to ten times higher than polymeric membranes[124] but can be brittle and expensive to produce. MMMs offer the ease of use associated with polymer membranes while also taking advantage of the superior separation ability of the inorganic material.

MOFs are crystalline materials with continuous regular structures[4, 5]. Many MOFs have been found to have highly porous structures [5-8] and therefore could be suitable for OSN separations. To overcome the issues associated with the fabrication of pure MOF films hybrid polymer/MOF membranes (e.g. MMMs) could be produced utilising the flexibility and mechanical strength of polymer membranes while incorporating the separation potential of MOFs.

The following chapter investigates the application of MMMs comprising of MOFs (HKUST-1) dispersed in asymmetric P84 polymer membranes for use in OSN applications. There are several challenges to creating mixed matrix membranes for OSN application. These include avoiding the formation of non-selective voids and ensuring the MOF particles are sufficiently near the membrane surface to facilitate transport through the selective layer of the membrane.

Polyimide membranes resistant to aprotic solvents such as DMF have been fabricated via the process of cross-linking[63, 64]. The properties of polyimide membranes can also be controlled by altering parameters such as membrane casting thickness, annealing time and solvent/co-solvent ratio[3, 116]. Therefore polyimide P84 was selected both due to its chemical stability in organic solvent, and the possibility to fabricate nanofiltration membranes from the polymer. The MOF selected in this chapter is HKUST-1, also known as Cu₃(BTC)₂. HKUST-1 was selected as it is one of the most widely studied and understood MOFs [4, 131] and can be readily fabricated copper salts and 1,3,5-benzene tricarboxylic acid and has a distinct and recognisable X-ray powder diffraction pattern. HKUST-1 can also be bought prefabricated from Sigma Aldrich as Basolite C300.

3.1.1 Improving the Compatibility of HKUST-1 and Polyimide P84 in Mixed Matrix Membranes

Mixed matrix membranes (MMMs) comprised of polymers and metal organic frameworks (MOFs) have been used for gas separation applications[48, 137, 139, 156, 157] but performances have not been optimal due to the presence non-selective voids between the polymer and MOF phases. These non-selective voids make MMMs particularly unsuitable for liquid applications. Adaption of the crystals in MMMs and the addition of fillers has been shown to improve polymer/inorganic adhesion and improve performance in gas separations[156, 210], this has also been used to improve separation in OSN applications[70].

The use of hexamethylenediamine (HDA) as a crosslinking agent was investigated as a way to improve adhesion between the HKUST-1 particles and P84 polymer chains. HDA is already used as a
crosslinking agent for P84 membranes. The amine functional group in the HDA can interact with HKUST-1, chemically bonding the MOF crystals to the polymer chains around them.

3.1.2 The Influence of MOF Loading on Mixed Matrix Membranes Structure and Performance

MOF loading has been shown to influence the permeation properties of MMMs used for gas separation applications[156, 163], and MMM/thin film composite (TFC) membranes used in OSN applications[70]. Increased MOF loading was shown to improve permeances in dense polymer membranes containing a range of MOFs. For TFCs containing MOFs embedded in a selective layer PDMS layer the solute rejections were found to improve with increasing MOF loading. Integrally skinned asymmetric HKUST-1/Polyimide P84 nanofiltration mixed matrix membranes were fabricated with HKUST-1 loading ranging from 5wt% to 50wt%. While increasing the percentage of MOF in MMMs might improve membrane performances, with increased particle loading there is more chance of particle agglomeration, and the formation of non-selective voids between MOF particles and polymer matrix.

In this chapter the permeance and rejection performances of the crosslinked and non-crosslinked MMMs with different MOF loadings were tested using polystyrene solute markers in acetone solvent. The membranes were characterised using X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) and ATR-FTIR. Changes in the thickness, mass and density of the membranes were also measured.

3.1.3 The Use of Non-Porous Carbon as Inorganic Fillers in Mixed Matrix Membranes

Asymmetric MMMs containing MOFs are designed to augment the separation properties of polymer OSN separation membranes. The regular porous nature of the MOFs are intended to improve separations either by improving the rate of permeation through the membranes (as seen with gas separation membranes), or improving solute retentions (as seen with MMM/TFCs). The changes may be attributed to the porous nature of the MOF particles or be due to changes in the membrane that occur during the phase inversion process.

Inorganic particles have been added to polymer membranes in order to alter their morphology and improve permeance performances. Titanium dioxide was been added to integrally skinned asymmetric polymer membranes to produce MMMs used to combat flux decline in OSN[147]. Another inorganic material, organosiloxane, has also been used to reduce the effect of flux decline in OSN membranes[71]. Gold nanoparticles have also been added to polyimide OSN membranes with a view to improving the flux of the membranes[211].

Whether the permeation performances of MMMs are influenced by the porous nature of the MOF particles or by changes in the morphology of the membranes containing inorganic fillers was tested using a non-porous filler of a similar size. Graphite, purchased from Sigma Aldrich was used to create crosslinked MMMs with a range of loadings from 5% to 50%, and compared to the crosslinked MMMs containing HKUST-1.
3.1.4 Novel Approaches to Creating Mixed Matrix Membranes with HKUST-1 in Asymmetric Polyimide P84 Nanofiltration Membranes

Formation of mixed matrix membrane dope solutions requires mixing steps to ensure that the discrete inorganic particles are distributed evenly throughout the final membrane. Issues with particle agglomeration, non-selective voids and positioning of the particles can all affect the final performance of MMMs.

Non-selective voids occur in MMMs when MOF crystals are especially large and/or agglomeration occurs. To avoid the issues associated with large particulate size and crystal agglomeration, HKUST-1 particles were fabricated within polymer dope solutions. Rather than adding pre-formed particles to dope solutions and mixing, the particles will form as the polymer is dissolved in solvent. Nanoparticle sized HKUST-1 crystals can be grown at room temperature in using ultrasonic waves. Due to their size these particles are difficult to separate from the solutions in which they are grown. Therefore growing these crystals in the dope solution would render separation of the particles unnecessary.

The morphology of the MMMs formed using this methodology was assessed using SEM analysis.

3.1.5 Chapter Aims

This chapter aims to explore the effect of MOF addition to polymer OSN separation membranes via the fabrication of MMMs. MMM fabrication is the simplest methodology to produce hybrid polymer/MOF membranes, however there are a number of issues that may need to be overcome to produce MMMs effective in OSN applications. This chapter will investigate the effectiveness of crosslinking molecules to improve adhesion between polymer and MOF phases, the effect of MOF loading in MMM and the influence of the porosity of MMM, using non-porous carbon particles as a control. The work should produce MMMs, consisting of MOF particles embedded in asymmetric polymer membranes, suitable for use in OSN applications. The morphology of these membranes, their chemical nature and the performance of these MMMs will be measured and assessed.

3.2 Experimental

3.2.1 Materials

Polypropylene non-woven backing was supplied by Viledon, Germany. Polyimide polymer (Polyimide P84) powder was purchased from HP Polymer GmbH, Austria. Solvents used for membrane preparation and membrane testing including isopropyl alcohol (IPA), acetone, dimethylformamide (DMF), ethanol (99.7%) and polyethylene glycol (MW 400) (PEG-400) were obtained from VWR International. Octanol was purchased from Sigma Aldrich. Hexane-1,6-diamine for crosslinking was purchased from Sigma Aldrich. Copper nitrate trihydrate, copper acetate monohydrate and 1,3,5-benzenetricarboxylic acid used for HKUST-1 fabrication were purchased from VWR International. HKUST-1 powder was supplied by Sigma Aldrich under its commercial name Basolite C300. Graphite Powder was supplied by Sigma Aldrich. Polystyrene markers for solute rejection evaluation were purchased from Agilent Technologies, UK.
3.2.2 Fabrication of Metal Organic Framework HKUST-1

The two solvothermal synthesis methods outlined by Chowdhury et al.[212] were used to synthesise HKUST-1.

Low temperature synthesis

1 g of benzene tricarboxylic acid (BTC) was dissolved in 30 ml of a 1:1 mixture of ethanol/DMF and mixed until the solute had completely dissolved. A mass of 2.077 g of hydrated copper (II) nitrate was dissolved in 15 ml of distilled water. The two mixtures were then mixed together and placed in an autoclave reaction vessel overnight at 100 °C. The resulting crystals were filtered. Any solvated DMF was removed using methanol in a Sohlext extractor. The crystals were then dried for an hour in an oven at 50 °C.

High temperature synthesis

A mass of 0.9832 g of BTC was added to 10 ml of ethanol and mixed until completely dissolved. A mass of 2.24 g of hydrated copper (II) nitrate was dissolved in 5 ml of distilled water, and added to the BTC solution. The resulting mixture was then stirred for 5 hours until completely mixed. The mixture was then heated in an autoclave for 48 hours at 140 °C. The resulting crystals were filtered and then dried overnight in an oven at 100 °C.

3.2.3 Membrane Fabrication

To produce integrally skinned nanofiltration membranes dope solutions were formed by dissolving 24 wt% of polyimide P84 in DMF/dioxane mixtures. The solvent/co-solvent ratio was 3:1, DMF:dioxane. This ratio of solvents ensured that the membranes had solute retentions in the nanofiltration range[3]. The dope solutions were cast on to polypropylene non-woven sheets using a casting knife set to a thickness of 250 μm (or 300 μm), in a controlled environment with a temperature of 20 °C and a humidity of 30–40%. The nanofiltration membranes were then precipitated from solution via immersion in water. The membranes were then placed in IPA to remove water from the polymer matrix. The membranes were submerged in 30 g.L⁻¹ solutions of hexane-1,6-diamine (HDA) in IPA for 20 hours for crosslinking. 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 hours. Uncrosslinked polyimide nanofiltration membranes were produced following the same procedure, however the crosslinking step with HDA was skipped.

Asymmetric MOF MMM nanofiltration membranes were prepared by dispersing HKUST-1 particles, purchased from Sigma Aldrich (average size 16 μm), or fabricated, in P84 dope solutions with 24 wt% of polymer in a mixture of DMF and dioxane. The ratio of DMF to dioxane was 3 :1, which ensured that the membranes produced had rejections in the nanofiltration range. The HKUST-1 particles were mixed into the dope solution as the P84 polymer dissolved. Mixing was undertaken in a sealed container to ensure no moisture was absorbed into the dope solution. The dope solutions were cast on to polypropylene non-woven sheets using a casting knife set to a thickness of 250 μm (or 300 μm). The MMMs were then precipitated from solution via immersion in water. The membranes were then placed in IPA to remove water from the polymer matrix. For crosslinked MMM, the membranes were submerged in 30 g.L⁻¹ solutions of HDA in IPA for 20 hours. Non-crosslinked membranes
skipped this step. After crosslinking the membranes were washed with IPA to remove excess crosslinking agent. Before testing all membranes were conditioned with a PEG400:IPA (60:40 v/v) solution for 12 hours.

Crosslinked MMM containing graphite particles, supplied by Sigma Aldrich, were fabricated using the same methodology employed to produce MOF MMMs.

*Table 3* details the composition of the membranes used to study the effect of crosslinking HKUST-1 MOF particles.

**Table 3**: List of polymer membranes and hybrid MMM fabricated to test the effect of particle crosslinking in MMM

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Dope Solution Composition</th>
<th>Filler</th>
<th>Polymer Crosslinking</th>
</tr>
</thead>
<tbody>
<tr>
<td>P84-NXL(300)</td>
<td>24% - P84 57% - DMF 19% - Dioxane</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>P84-XL(300)</td>
<td>24% - P84 57% - DMF 19% - Dioxane</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>MMM-NXL(300)</td>
<td>24% - P84 57% - DMF 19% - Dioxane</td>
<td>1.2g of HKUST-1</td>
<td>No</td>
</tr>
<tr>
<td>MMM-XL(300)</td>
<td>24% - P84 57% - DMF 19% - Dioxane</td>
<td>1.2g of HKUST-1</td>
<td>Yes</td>
</tr>
<tr>
<td>MMM-PXL(300)</td>
<td>24% - P84 57% - DMF 19% - Dioxane</td>
<td>1.2g of Pre-Crosslinked HKUST-1</td>
<td>No</td>
</tr>
</tbody>
</table>

Each membrane was made using a 50g dope solution. Laboratory fabricated HKUST-1 crystals were added to DMF/Dioxane mixtures and sonicated to prevent particle agglomeration. Polyimide was then added to the mixture and dissolved using a magnetic stirrer to make the dope solutions from which the membranes were cast from. The membranes were all cast at a thickness of 300 μm. All the membranes were made using phase inversion via immersion precipitation in a water bath at room temperature.

The membranes used to test the effect of MOF loading in asymmetric MMMs contained HKUST-1 purchased from Sigma Aldrich. The non-crosslinked membranes used were NXL0, NXL5, NXL10 and NXL20, where NXL stands for non-crosslinked and the number refers to the percentage of MOF loading in the membranes. The crosslinked membranes used were XL0, XL5, XL10, XL20 and XL50, where XL stands for crosslinked and the number refers to the percentage loading of MOF in the membrane.

Novel asymmetric MMMs were fabricated by dissolving HKUST-1 precursors (copper nitrate or copper acetate and benzene tri-carboxylic acid) in DMF solvent. 24 wt% of P84 polymer was
dissolved into the solution in a sealed container. Once the P84 was dissolved the dope solutions were submerged in an ultrasonic bath to encourage the growth of HKUST-1 particles.

3.2.4 X-Ray Powder Diffraction (XRPD)

X-ray powder diffraction patterns were acquired at room temperature on a PANalytical X'Pert Pro diffractometer using CuKα radiation (1.541 Å), with a Nickel filter, a fixed 10 mm mask, a 0.04 rad soller slit and divergence and antiscatter slits of 1/4° and 1/2° respectively. The data was collected between a 5 to 40° angular range in 2θ in continuous scan mode using a step size of 0.05° and a step time of 5 s.

3.2.5 Scanning Electron Microscopy

The cross-sections of the membranes, P84-NXL(300), P84-XL(300), MMM-NXL(300), MMM-XL(300) and MMM-PXL(300) were characterized by low resolution scanning electron microscopy (SEM), as were the MMMs fabricated with HKUST-1 growth in the dope solution. The samples were coated with gold under an argon atmosphere using an Emitech K550X peltier in order to make the samples conductive. The microscopic analyses were performed using a JMC-5700, Jeol SEM at 20kV.

The cross-sections of the other membranes used in this chapter were characterized by high resolution scanning electron microscopy (SEM). The samples were coated with chromium under an argon atmosphere using an Emitech K575X peltier in order to make the samples conductive. The microscopic analyses were performed at 5 kV in a high resolution LEO1525 Karl Zeiss SEM.

3.2.6 Membrane Mass, Density and Thickness Measurements

Samples (area: 3 cm x 3 cm) were taken from each membrane and their thicknesses measured using a Mitutoyo electronic thickness gauge. The samples were then washed with acetone to remove PEG conditioning agent. The removal of PEG conditioning agent was confirmed using ATR-FTIR. The acetone was then dried from the membrane at room temperature. The mass of each sample was then measured using an electronic scale. The thickness and mass of the polypropylene non-woven backing was measured and subtracted from the thicknesses and masses of the membrane samples in order to find the dimensional parameters of the membrane alone.

3.2.7 ATR-FTIR

Fourier Transform-Infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrometer 100, with samples mounted on a zinc-selenium/diamond plate. The spectra were collected in the attenuated total reflection (ATR) mode, directly from the membrane surface. The spectra were recorded at a resolution of 4 cm⁻¹ as an average of 16 scans. The membranes were washed in acetone to remove any contamination and dried before analysis.

3.2.8 OSN Experimental Procedure

Filtration experiments were carried out using either a cross-flow filtration system (schematic shown in Figure 3) or a dead end filtration cell (shown in Figure 4). The effective area of each membrane was 14 cm². For cross flow tests at least 2 discs of each membrane were placed in an 8 cell cross-flow rig, which comprises 2 parallel sets of 4 membranes in series. For the dead end cell experiments, at least 2 discs of each membrane were also used except for membrane P84-XL(300),
for which the results of only one disc was used as all the other discs tested contained pinholes. The membranes tested in the cross-flow filtration system were tested for 24 hours in order to ensure a steady permeance had been reached. For dead-end cell experiments the initial volume of the solution was 100 ml and after 50 ml of permeate had been collected filtration was stopped. For the dead-end filtration test the average permeance over the whole filtration period was recorded. For the cross-flow filtration the final steady state membrane permeance was measured and recorded. The membrane permeance was calculated using **Equation 2**.

The model system for the solute rejection experiments comprised of a mixture of 1 g.L\(^{-1}\) PS580 and PS1300 polystyrene markers as well as 0.1 g.L\(^{-1}\) of methyl styrene dimer solution in acetone[37]. Membrane rejections were calculated using **Equation 3**.

For cross-flow filtration tests samples of polystyrene solution were taken from the feed and the permeate line of each of the membranes. For dead-end filtration tests samples of polystyrene solution were collected after the filtration was complete. The acetone was evaporated and the residue was re-dissolved in DMF. The HPLC analysis was based on the method previously reported by See-Toh et al.[85]. Analysis of the polystyrene markers was undertaken using an Agilent HPLC system equipped with UV/Vis detector set at a wavelength of 264 nm and a Phenomenex C18 (300A, 250x4.6 mm) reverse phase column.

**Figure 3**: Schematic diagram of the cross flow system. The system is pressurised by a pump, which also circulates the solution. The system temperature is control by a heat exchanger, which uses the temperature probe to set the flow rate of a cooling water supply. The system also contains a pressure sensor and a flowmeter.
Figure 4: Diagram demonstrating the operations of a dead end cell unit. The system is pressured by inert nitrogen gas.

3.3 Results and Discussion

3.3.1 Fabrication of Metal Organic Framework HKUST-1

A light blue powder was obtained from the high temperature HKUST-1 synthesis methodology; a bright blue powder was obtained from the low temperature HKUST-1 synthesis. The two materials were tested using XRPD to assess the structure of the compounds and to determine if HKUST-1 had been produced.

The results from the XRPD of the compounds produced by the different synthesis methods are shown in Figure 5.

The graphs have completely different peak positions, indicating that the compounds themselves are different. Comparing these results to literature XRPD data for HKUST-1 it can be seen that the material produced by low temperature synthesis has peaks at the same 2\(\theta\) angle as HKUST-1. The results from the XRPD of the high temperature synthesis indicate that the material produced was not HKUST-1. XRPD data displayed in literature shows prominent peaks at around 2\(\theta\) angles 6.5°, 9.5° and 11.5°[133, 183, 212-215] for HKUST-1, these can be seen in the results produced via low
temperature synthesis (see Figure 5), the results obtained by Panella et al. [213] and the results obtained by Schlichte et al. [183]. It is likely that due to the small volume of solvent used the BTC never fully dissolved in the ethanol, leaving unreacted BTC in the solution. The compound produced by the high temperature synthesis is unknown and was likely formed due to experimental error, as the BTC was likely not fully dissolved. However as the low temperature synthesis produced HKUST-1 crystals suitable for use in MMMs, and MOF fabrication was not the focus of this thesis further investigation of the high temperature synthesis was not carried out.

Figure 5: XRPD data from crystals formed by solvothermal synthesis using high temperature and low temperature synthesis routes as described by Chowdhury et al. [212]

Excess reaction solution from the low temperature synthesis method was left at room temperature for 48 hours. Blue crystals, similar to the crystals found in the autoclave after solvothermal synthesis, had formed at the bottom of the flask. The formation of metal organic frameworks is thermodynamically favourable but slow. During the solvothermal synthesis all the reactants were spent and the remaining solvent was colourless. The solution left to form HKUST-1 at room temperature still had a pronounced blue colour after several days. This proves that room temperature synthesis of HKUST-1 is possible; however the process is slower than solvothermal processes.
Figure 6 shows that HKUST-1 can be formed using a solvent mixture of water/DMF/ethanol, DMF/ethanol and just ethanol. Each of the crystals formed in different solvent mixtures exhibit the characteristic peaks of HKUST-1. This work also confirms that HKUST-1 can be readily fabricated at room temperature.

3.3.2 Improving the Compatibility of HKUST-1 and Polyimide P84 in Mixed Matrix Membranes

After exposure to Hexane-1,6-diamine (HDA) in isopropanol solution, HKUST-1 crystals were found to have gained significantly in weight (>50%). The crystals also exhibited a change in colour from a bright turquoise to a darker shade of blue (shown in Figure 7). Colour changes in HKUST-1 crystals are associated with changes in the co-ordination state of the copper ions, often when species bond with the free electron pairs. The colour change and weight gain could indicate that HDA molecules are adsorbing on to the internal surfaces of the porous structure of the HKUST-1, or the external surface of the crystals. As HDA is a reactive with polyimide P84, the addition of the molecule to the HKUST-1 crystals could aid adhesion to the polymer.

Figure 7: Colour change of HKUST-1 crystals after HDA adsorption
The MWCO curves for the polymer nanofiltration membranes and MMM nanofiltration membranes can be found in Figure 8. The polymer membranes P84-NXL(300) and P84-XL(300) are used as a control experiment. It can be seen from the rejection results of these membranes that the non-crosslinked membrane P84-NXL(300) has higher solute retentions than the crosslinked P84-XL(300) membrane. Therefore any improvement in the rejection of the MMMs after crosslinking should not be due to changes in the polymer. The permeance data for the membranes, which can be found in Table 4 shows that crosslinking the polymer membranes has a detrimental effect on the permeance of the polymer membranes, which drops from 28 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) to 6.3 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\).

![Figure 8: MWCO of MMMs and traditional membranes with polystyrene in acetone solvent at 20 bar applied pressure in a dead end cell. Mean data for each membrane plotted, error bars show one standard deviation](image)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeance (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P84-NXL(300)</td>
<td>28</td>
</tr>
<tr>
<td>P84-XL(300)</td>
<td>6.3</td>
</tr>
<tr>
<td>MMM-NXL(300)</td>
<td>37</td>
</tr>
<tr>
<td>MMM-XL(300)</td>
<td>5.5</td>
</tr>
<tr>
<td>MMM-PXL(300)</td>
<td>25</td>
</tr>
</tbody>
</table>

The MWCO curve for the uncrosslinked MMM-NXL(300) shows that the membrane has a maximum solute rejection that plateaus at around 40%. The membrane rejection also displays a large error range. The low membrane rejection, plateaued MWCO curve and a large range of solute rejections
is symptomatic of the effect of non-selective voids, large voids between the MOF and the polymer, which allow the all molecules through. When a significant number of non-selective voids exist in a membrane the measured rejection is a ratio between the rate at which molecules can transport through the non-selective voids and the rest of the membrane. The membrane MMM-NXL(300) has a higher rejection than the non-crosslinked polymer membrane, however, the low solute retentions of the MMM indicate that this is most likely due to the presence of non-selective voids in the membrane.

The addition of HDA crosslinking to the membrane, post HKUST-1 addition improves the observed rejection polystyrene of solutes. Solute rejections for the MMM-XL(300) are 40% to 45% higher than the MMM-NXL(300), however, the highest rejection on the MWCO still plateaus at around 85%. This suggests that the membrane still contains non-selective voids, but the voids are either smaller, or less frequent. The permeance of the crosslinked membrane, MMM-XL(300) was much lower than the non-crosslinked membrane, MMM-NXL(300). Crosslinking also had a detrimental effect on the permeance of the polymer membranes, and therefore the reduction in permeance could be due to changes in the permeance through the polymer phase of the membrane. The crosslinked mixed matrix membrane MMM-XL(300) has a slightly lower permeance (5.5 L m⁻² h⁻¹ bar⁻¹) than the crosslinked polymer membrane P84-XL(300) (6.3 L m⁻² h⁻¹ bar⁻¹). The lower permeance could be due to the HKUST-1 particles having a lower permeance than the polymer phase of the membrane, or due to blocking of the HKUST-1 pores by HDA molecules. MMM-XL(300) had higher solute retentions than P84-XL(300), demonstrating that HKUST-1 has the ability to improve solute retentions in MMMs.

HKUST-1 crystals pre-treated with HDA were used to further improve adhesion between the polymer phase and the MOF crystals within MMMs. MMMs created using pre-crosslinked HKUST-1 (MMM-PXL(300)) displayed improved retentions for solutes of low molecular weight. The permeance of the membrane was higher than MMM-XL(300), as the crosslinking agent was not added to the polymer phase of the membrane. A permeance of 25 L m⁻² h⁻¹ bar⁻¹ is close to the value obtained for the non-crosslinked polymer membrane (P84-NXL(300)). However as the solute retentions are higher the additions of pre-crosslinked HKUST-1 to membranes could be said to improve the performance of this membrane.

Despite the improved performance of the membrane, using pre-crosslinked HKUST-1 particles caused issues during membrane fabrication. Crosslinking between MOF crystals caused some particles to agglomerate in the dope solution. Once the membrane was cast some areas of the membrane were unsuitable for use. Sonication was used to reduce particle agglomeration, however, if the dope solutions were sonicated for too long HDA would detach from the HKUST-1 particles and crosslink the polymer before the membrane had been cast.

**Figure 9** shows SEM images of the cross-sections of the crosslinked and non-crosslinked MMMs. While the images do not show the membrane selective layers, the images shown are meant to demonstrate the adhesion between MOF particles and the polymer phase throughout the membrane. SEM images cannot give a quantitative assessment of number and size of non-selective voids, but are used purely as a qualitative tool. The SEM image of the non-crosslinked MMM-NXL(300), A, shows a MOF particle embedded in the polymer, surrounded by large voids between the polymer and membrane. This SEM image is demonstrative of the voids which could cause the
membrane to perform poorly. The SEM of the membrane, MMM-XL(300), shows a particle embedded in the polymer matrix of a P84 membrane, though non-selective voids can be seen at the edges of the particle they are much smaller than those present in the non-crosslinked MMM, MMM-NXL(300). The final SEM images, C & D show images of the pre-crosslinked HKUST-1 particle embedded into the polymer matrix of the membrane, MMM-PXL(300), in these SEM images no non-selective voids can be seen.

![Figure 9: SEM images of HKUST-1 particles embedded into polymer matrix of MMMs (A) MMM-NXL(300), (B) MMM-XL(300) and (C & D) MMM-PXL(300)](image)

3.3.3 The Influence of MOF Loading on Mixed Matrix Membranes Structure and Performance

Different loadings of HKUST-1 were added to polymer dopes to produce MMMs. Changes in the physical parameters of the resulting membranes were measured and are shown in Figure 10. The thickness of the crosslinked membranes was found to be higher than the non-crosslinked membranes. For the non-crosslinked membranes, HKUST-1 addition increases the thickness of the membranes; however there is no trend between MOF loading and thickness. There appears to be no trend in thickness for the non-crosslinked membranes, from 0% to 20%, however the crosslinked MMM containing 50% HKUST-1, XL50, has a significantly higher thickness than the other membranes.

As with the thicknesses, the mass of the crosslinked membranes are higher than the non-crosslinked membranes. With the non-crosslinked membranes the mass of the membranes increase with increasing MOF loading. The trend for the crosslinked membranes also increases, except membrane XL10. Finally the densities of the crosslinked and non-crosslinked membranes appear largely similar, and for each set of membranes the densities of the MMMs increases with increasing MOF loading.
The density of HKUST-1 is 1.22 g cm\(^{-3}\) [216], this is higher than the density of the pure polymer NXL0 and XL0 membranes, 0.72 g cm\(^{-3}\) and 0.64 g cm\(^{-3}\) respectively. Therefore it should be expected that with increased MOF loading the density of the MMMs should increase. The addition of MOF filler particles to MMM dope solutions could alter the phase inversion process, changing the density of the polymer phase of the membranes.

**Figure 10:** Thickness, Mass and Density measurements of Non-crosslinked (NXL-) and crosslinked (XL-) membranes, the number in the membrane name refers to the mass percentage of HKUST-1 added to the membrane dope solution.

XRPD data for the membranes can be found in **Figure 11**. The peaks of the HKUST-1 signal can be seen to get stronger with increasing MOF loading. The largest HKUST-1 peak, at 12.5°, was used to plot the increasing intensity of the MMM plots. It can be seen that intensity of the peaks is higher in non-crosslinked MMMs than the crosslinked MMMs. These XRPD patterns confirm that HKUST-1 is embedded in the structure of the polymer.
**Figure 11:** (Left) XRPD patterns for the NXL- and XL- membranes, the MMMs show characteristic peaks of HKUST-1 powder. (Right) The intensity of the largest HKUST-1 peak (12.5°) is compared to the percentage of HKUST-1 powder added to the membrane.

**Figure 12:** ATR-FTIR data for the surface of (Left) the non-crosslinked and (Right) the crosslinked membranes. The ATR-FTIR signals for non-crosslinked polymer membranes and the MMMs are indistinguishable from each other, and the FTIR data does not follow that of HKUST-1 powder, except at the point of two peaks. The FTIR data for the crosslinked membranes also follows the same pattern, and the membranes are indistinguishable from one another. The crosslinked MMMs do not share any peaks of the HKUST-1 powder. ATR-FTIR can penetrate materials up to 5 microns in depth, so though the HKUST-1 material is located in the MMM, the MOF crystals are not often found at the membrane surface.

**Figure 13** shows SEMs of the crosslinked MMMs. It can be seen that with increasing MOF loading, the macrovoids at the bottom of the membranes become more tortuous and for the membrane XL50 the number of macrovoids has visibly decreased.
Figure 13: SEM images of cross-section of (A1/2) XL0, (B1/2) XL5, (C1/2) XL20, (D1/2) XL50 membrane, showing the effect of increasing HKUST-1 powder
Figure 14: Polystyrene rejection for (Left) the non-crosslinked and (Right) the crosslinked membranes (acetone solvent, 10 bar)

Figure 15: Permeance data for (Left) the non-crosslinked and (Right) the crosslinked membranes (acetone solvent, 10 bar)

Figure 14 shows the rejection data for the non-crosslinked and crosslinked polymer nanofiltration membranes and MMMs. For both the non-crosslinked and crosslinked membranes the solute retentions of the MMMS are only slightly higher than the polymer membranes. With increasing MOF loadings the average solute retentions of the MMMS increased. However, the differences observed between the membranes were all within the one standard deviation (shown with the error bars), indicating that the observed increases are not significant. The retentions of the non-crosslinked MMMS do not appear to be affected by the presence of non-selective voids, as previously shown when using laboratory fabricated HKUST-1 particles. This could be because the HKUST-1 particles used were different from the laboratory fabricated particles used in the previous study. The HKUST-1 particles supplied by Sigma Aldrich appear to have much better adhesion between the polymer and MOF phases, as shown in by the SEM images in Figure 13 and the rejection results in Figure 14.

Figure 15 shows the permeance for both non-crosslinked and crosslinked membranes. The permeances of the non-crosslinked MMMS are similar to, or slightly greater than the non-crosslinked
polymer membranes, though there is no trend between MOF loading and permeance. For the crosslinked membranes the permeance of the MMMs is significantly lower than that of the polymer membrane. The permeance of the MMMs decreases continually with increased MOF loading.

While MOF loading in membranes has been shown to affect the morphology of the MMMs formed surprisingly there is very little difference between the performances of MMMs with 5 wt% HKUST-1 and 50 wt% HKUST-1. The ATR-FTIR results indicate that there is very little, if any, HKUST-1 directly at the surface of the MMMs, therefore increases in the MOF loading may not have a profound influence on the selective layer of the membrane.

3.3.4 The Use of Non-Porous Carbon (Graphite) Particles in Mixed Matrix Membranes

![Graph showing rejection vs molecular weight for MMMs with different carbon loadings](image)

**Figure 16**: Polystyrene rejection for crosslinked MMM containing carbon particles tested at 10 bar with polystyrene in acetone solvent. Mean data for each membrane plotted, error bars show one standard deviation

MMMs containing particles of non-porous graphite were produced as a control to test how the porous nature of MOF fillers may affect the performance of MMMs. Graphite particles, purchased from Sigma Aldrich were selected as they had an average size similar to the HKUST-1 particles (average size 16 µm). As graphite and HKUST-1 are both carbon based materials the adhesion between the polymer and the particles should be similar in both cases.

Rejection data for carbon based MMMs can be found in **Figure 16**. As with the crosslinked MOF based mixed matrix membranes there is a slight, if insignificant increase in rejection for the carbon based MMMs. However there appears to be no trend in increasing rejection with increasing carbon
loading. As the carbon particles are non-porous in nature, the slight increase in rejection must be due to changes in the properties of the polymer phase of the membranes.

The permeance data for the carbon based MMMs can be found in Figure 17. As with the HKUST-1 MMMs the permeance of the carbon based MMMs is lower than that of pure polymer membranes. The permeances of the MMMs follow no trend based on carbon loading. The permeance of the carbon based MMMs are all close to 20 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), similar in permeance to the membranes XL5 and XL20, though around twice the permeance of XL50. This result is surprising as it would be reasonable to expect that the porous nature of the HKUST-1 would improve permeance through the MMMs. This result implies that the pores in crosslinked MMMs can become blocked by the presence of HDA crosslinking agent.

Figure 18 shows the cross-sections of the carbon based MMMs. As with the MOF MMMs increased particle loading increased the tortuosity of the macrovoids in the membrane, and also reduced the number of macrovoids grown. The carbon particles appear to have good adhesion to the polymer phase of the membranes, and non-selective voids are rare.

Both morphologically and performance wise there appears to be very little difference between crosslinked MMMs fabricated using carbon particles and MOF. The membranes have similar rejection and permeance performances, indicating that the pores of the particles in the MMMs are not facilitating solvent transport.
Figure 18: SEM images of carbon MMMs containing from to bottom increasing amounts of carbon particles by weight; (top row) 5%, (middle row) 20% and (bottom row) 50%.

3.3.5 Novel Approaches to Creating Mixed Matrix Membranes with HKUST-1 in Asymmetric Polyimide P84 Nanofiltration Membranes

As a methodology to decrease the size of the HKUST-1 crystals, improve polymer/MOF adhesion and possibly improve the positioning of MOF particles in MMMs, HKUST-1 was grown within membrane dope solutions. This was achieved by adding HKUST-1 reagents to dope solution mixtures and using ultrasonic baths to encourage MOF growth.

Figure 19 shows the structure of a typical MMM, produced by adding pre-fabricated HKUST-1 crystals to a dope solution of 24 wt% P84 in DMF solvent. An asymmetric MMM was formed with
HKUST-1 distributed throughout the membrane cross-section. Non-selective voids are visible and very few crystals can be seen at the membrane surface.

Figure 19: Cross-section (top) and surface (bottom) of standard MMM

To produce the membrane seen in Figure 20 hydrated copper nitrate, benzene tricarboxylic acid and polyimide P84 were dissolved in DMF. The dope solution was sonicated and heated to encourage crystal growth.

Figure 20: Cross-section (top) and surface (bottom) of copper nitrate based MMM
It can be seen in Figure 20 that this membrane has large holes throughout the cross-section and surface of the membrane. Water from the hydrated copper nitrate will have disassociated from the copper nitrate as it dissolved in solution and reacted and this water could be the cause of the formation of large holes throughout the membrane. These large holes make the membrane unsuitable for OSN applications.

The final MMM was produced by dissolving copper acetate, benzene tricarboxylic acid and polyimide P84 in DMF. The dope solution was sonicated to encourage crystal growth. The resulting membrane can be seen in Figure 21.

![Figure 21](image)

**Figure 21:** Cross-section (top) and surface (bottom) of copper acetate based MMM

A spongy membrane with a high density of HKUST-1 crystals near the surface of the membrane was formed. The crystals are also smaller than prefabricated HKUST-1 crystals and there are no visible non-selective voids.

The membrane shown in Figure 21 was tested in OSN conditions; however the rejections achieved were extremely low (0-5% for all polystyrene markers in acetone). This is likely due to the fact the membrane dope solution contained no co-solvent, only DMF. Addition of co-solvents to dope solution mixtures has been shown to increase the rejection of P84 membranes into the nanofiltration range. Attempts to recreate the membrane using a mixture of DMF and dioxane were not successful as the presence of the dioxane inhibited the dissolution of the BTC compound, and the MOF fabrication reaction could not occur.
3.4 Conclusions

Asymmetric MMMs containing MOF particles were produced and used in OSN applications. However the applicability of these membranes was variable. The performance of the MMMs was mostly dependent on whether laboratory or purchased HKUST-1 was used.

HKUST-1 was shown to be able to be produced at ambient temperatures (<25 °C). However HKUST-1 particles purchased from Sigma Aldrich, AKA Basolite C300 were preferred for most experiments as MMMs containing these particles did not form non-selective voids in the membranes. Differences in crystal particle size distribution, and MOF solvent content could affect the adhesion between the polymer and MOF phases, as well as the separation capabilities of the MOF particles themselves. Different fabrication methodologies could lead to differences between Basolite C300 and lab-grown HKUST-1 that influence the incorporation of the particles into the polymer matrix. One key difference between the laboratory fabricated HKUST-1 and the Basolite C300 purchased from Sigma Aldrich can be observed in the SEM images, the shape of the crystals. While the Basolite C300 particles (as seen in Figure 13) are regular and mostly tetragonal in shape, the laboratory fabricated HKUST-1 crystals are irregular (see Figure 9). The presence of irregular shapes of the laboratory fabricated crystals could cause the formation of non-selective voids during the phase inversion process.

Rejection data and SEM images suggest that HDA could be used to reduce the effect of non-selective voids in MMMs containing P84 and laboratory fabricated HKUST-1. However the crosslinking agent could be blocking the pores of the MMMs, leading to lower permeances than those achieved for pure polymer nanofiltration membranes and non-crosslinked MMMs. Pre-crosslinking of HKUST-1 was shown to improve both the rejection and permeance of MMMs as compared to post-crosslinking processes. However this route means that the polymer membrane is not crosslinked, reducing the solvent stability of the membrane.

Experiments using Basolite C300 purchased from Sigma Aldrich show that MOF loading had no significant influence on the rejection performances of MMMs. ATR-FTIR data shows that there is no MOF at the surface of the MMMs, and therefore the HKUST-1 will not be found in the selective layer of the membranes. For crosslinked MMMs the permeance decreases with increasing MOF loading, whereas the opposite is true for non-crosslinked MMMs. The difference in permeance could be explained by the HDA crosslinker blocking the pores of the HKUST-1 crystals when they adsorb on the surfaces of the MOF crystals. Filtration results of MMMs containing non-porous carbon particles are very similar to the results obtained for the crosslinked MMMs containing HKUST-1. This indicates that the HKUST-1 particles may become non-porous in the presence of HDA.

As MOF particles are dispersed within a continuous phase of polymer in MMMs, and because there is no way to guarantee that MOF particles will orientate at the surface of the integrally skinned asymmetric membranes, the influence that MOFs can have on permeation in MMMs will always be restricted. Therefore to improve the performances of hybrid polymer/MOF membranes Chapter 4 explores the fabrication of in-situ growth (ISG) hybrid polymer/MOF membranes. To fabricate these membranes continuous MOF phases will be grown within the pre-existing pores of polymer membranes. This should ensure that the MOF phase will be present at the surface of the membrane, and should increase the influence of MOF on the separation properties of hybrid
membranes. As HKUST-1 was shown to be able to form at room temperature this means that the ISG membranes can be produced at temperatures that will not damage the polymer support membrane.
Chapter 4

4. Fabrication of Hybrid Polymer/Metal Organic Framework Membranes: Mixed Matrix Membranes versus In-Situ Growth

4.1 Introduction

As discussed in Chapter 4, the most common membranes used for OSN applications are polymer integrally skinned asymmetric (ISA) membranes. The most common preparation methodology for producing ISA membranes is phase inversion via immersion precipitation[2]. However control of the phase inversion process is imprecise, and membranes with predictable, regular porous structures cannot be obtained. Another negative aspect of ISA polymer membranes is flux decline, caused by pressure induced compaction and rearrangement of the polymer chains[71, 217]. Both flux decline and irregular porous structures have been obstacles to producing polymer OSN membranes with precise and predictable separation performances.

One approach to reduce flux decline has been to produce hybrid organic/inorganic membranes using a mixed matrix membrane (MMM) approach. This membrane fabrication methodology leads to the formation of hybrid membranes with discrete particles distributed in a continuous polymer phase. As MMMs contain discrete particles of MOF in a continuous polymer network, the permeation flow path through these membranes is a composite of both the polymer and MOF components of the membrane. For this reason, the influence the MOF phase can have on the separation properties of MMMs is limited.

Figure 22: Schematic representation of ISG membrane showing (a) the building block molecules used to create HKUST-1, Cu$^{2+}$ ions and benzene tricarboxylate, (b) a bird’s eye view of the HKUST-1 molecular structure showing the window into the MOF cage, (c) a 3D rendering of a HKUST-1 crystal, showing the network of cages and (d) HKUST-1 crystals (blue) grown within the porous top layer of a polymer membrane (yellow)
To improve upon the performance of hybrid polymer/MOF membranes, this chapter introduces a novel membrane fabrication method for OSN, *in-situ* growth (ISG), wherein MOF crystals are grown in pre-formed polymer membranes. Using ISG to produce hybrid polymer/MOF membranes should minimise the issues of polymer/MOF interface interaction associated with MMMs. By growing MOF crystals in the pre-existing pores of the polymer membrane, it is possible to grow a more continuous MOF phase, meaning that the transport properties of the ISG membrane are determined by the structure of the chosen MOF. Figure 22 shows a conceptual plan of MOF crystals grown in the top layer of a polymer membrane, transforming the membrane pores. The characteristics of these novel ISG membranes are tested with a number of analytical techniques (SEM, EDX, BET, AFM, XPRD, ATR-FTIR and water contact angle) to determine their structural properties. The novel ISG membranes are compared with MMMs and parallels are drawn between the membrane morphologies, permeance and rejection performance of the membranes.

In this chapter hybrid membranes containing the metal organic framework (MOF) HKUST-1 in an integrally skinned asymmetric polyimide membrane are fabricated with a view to testing the effect of the MOF on membrane performance and flux decline in OSN applications. HKUST-1 is one of the most widely studied and understood MOFs [4, 131] and can be fabricated at room temperature from copper nitrate and 1,3,5-benzene tricarboxylic acid, or bought from Sigma Aldrich as Basolite C300.

Polyimide P84 was selected as the polymer used to create the ultrafiltration support membranes due to its high stability in organic solvents. Crosslinked P84 membranes can even be made to be stable in polar aprotic solvents such as DMF and DMSO[1]. These solvents are often used during the synthesis of HKUST-1, so stability of the membrane in these solvents is important.

### 4.1.1 Chapter Aims

The current approach to produce hybrid Polymer/MOF membranes, MMMs, has been demonstrated to be adversely effected by the formation of non-selective voids and by the discrete nature of the MOF phase within these membranes. Chapter 2 demonstrated that the influence of HKUST-1 on permeation in integrally skinned asymmetric nanofiltration membranes is minimal. In order to avoid the issues associated with MMMs, MOFs are grown within the existing pores of polymer membranes via an approach known as *in-situ* growth (ISG). This chapter aims to demonstrate that ISG membranes have improved retention characteristics above that of MMMs. The morphological and chemical differences between ISG, MMM and polymer membranes will be explored using SEM, AFM, XRPD and FTIR and related to the membrane performances.

### 4.2 Experimental

#### 4.2.1 Materials

The materials used in this chapter are identical to those used in Chapter 3 (see section 3.2.1 Materials) with the addition of DMSO supplied by VWR International.

#### 4.2.2 Membrane Preparation

Polymer ultrafiltration (UF) membranes were produced via phase inversion (see Figure 23). Dope solutions were formed by dissolving 24 wt% of polyimide P84, herein referred to as P84, in DMF. The P84 and the DMF were mixed in a sealed container, while the polymer dissolved, to ensure no
moisture was absorbed into the dope solution. The dope solutions were cast on to polypropylene non-woven sheets using a casting knife set to a thickness of 250 μm, in a controlled environment with a temperature of 20 °C and a humidity of 30–40%. The polymer membranes were then precipitated from solution via immersion in water.

Figure 23: Schematic of membrane fabrication processes (A) UF membrane, (B) MMM and (C) ISG membrane; (A) shows the fabrication of a polymeric ISA membrane formed via phase inversion, the final membrane is purely polymeric with an irregular porous structure, (B) shows the fabrication of a MMM, pre-formed HKUST-1 crystals are added to the dope solution, producing a hybrid membrane with discrete particles of MOF in an irregular porous network, (C) shows the fabrication of the novel ISG membrane, where HKUST-1 is grown in-situ in the pores of the ISA membrane.

The membranes were then placed in IPA to remove water from the polymer matrix. For crosslinking, the membranes were submerged in 30 g.L⁻¹ solutions of hexane-1,6-diamine (HDA) in IPA for 20 hours. 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 hours. Uncrosslinked polyimide membranes (UF-NC) were produced following the same procedure however the crosslinking step with HDA was skipped. Crosslinked polyimide membranes were formed without macrovoids (UF-DMSO) by first dissolving 24wt% of P84 in DMSO solvent in a sealed container. The membrane was then cast in the same conditions and at the same thickness as the UF membrane cast from DMF. The post-casting membrane fabrication methodology for the UF-DMSO membrane is the same UF membrane, including crosslinking with HDA and conditioning with PEG400/IPA.

MMMs were prepared by dispersing HKUST-1 particles (average size 16 µm) in P84 dope solutions with 24 wt% of polymer in DMF (see Figure 23). The ratio of polymer to MOF by weight in the dope solutions was 5:1. The HKUST-1 particles were mixed into the dope solution as the P84 dissolved. Mixing was undertaken in a sealed container to ensure no moisture was absorbed into the dope solution. The dope solutions were cast on to polypropylene non-woven sheets using a casting knife set to a thickness of 250 µm. The MMMs were then precipitated from solution via immersion in water. The membranes were then placed in IPA to remove water from the polymer matrix. For crosslinking, the membranes were submerged in 30 g.L⁻¹ solutions of HDA in IPA for 20 hours. 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 hours.

Hybrid polymer/MOF in-situ growth (ISG) membranes were fabricated using polymer UF membranes as structural scaffolds (see Figure 23). ISG membranes were prepared by immersing the polymer UF membranes into a fresh mixture of copper nitrate (0.86 M in Ethanol solution) and 1,3,5-benzenetricarboxylic acid (0.40 M in DMF solution). The membranes were left stirring in solution for 24 hours, and were subsequently washed with DMF to remove any unreacted reagents. Before testing the membranes were conditioned with a PEG400:IPA (60:40 v/v) solution for 12 hours.

4.2.3 Membrane Characterization

Membrane mass, density and thickness measurements were carried out using the same methodology described in Chapter 3 (see section 3.2.6 Membrane mass, density and thickness measurements)

Fourier Transform-Infrared (FT-IR) spectra were recorded using the same Perkin-Elmer Spectrometer 100 instrument as described in Chapter 3 (see section 3.2.7 ATR-FTIR). PEG-400 conditioning agent was removed from the membrane samples before testing using acetone, similar to the membranes in Chapter 3.

Scanning electron microscopy (SEM) images were captured using a high resolution LEO1525 Karl Zeiss SEM at 5 kV, as described in Chapter 3 (see section 3.2.5 Scanning Electron Microscopy). Energy-dispersive X-ray spectroscopy (EDX) was carried out using the same LEO1525 Karl Zeiss SEM at 20 kV. In order to make the samples conductive samples were coated with chromium under an argon atmosphere using an Emitech K575X peltier.

The cross-sections of the membranes used to measure the effect of pressure on the membranes were characterized using low resolution scanning electron microscopy (SEM) using a JMC-5700, Jeol SEM at 20kV. Membrane samples were coated with gold under an argon atmosphere using an Emitech K550X peltier.
X-ray powder diffraction (XRPD) was carried out using the same PANalytical X’Pert Pro diffractometer used in Chapter 3 (see section 3.2.4 X-Ray Powder Diffraction), using the same step-size of 0.05° and a step time of 5s.

Contact angle measurements were performed with an Easy-Drop Instrument (manufactured by Kruess) at room temperature using the drop method, in which a drop of water was deposited on the surface of a membrane using a micropipette. The contact angle was measured automatically by a video camera using the drop shape analysis software. All membranes were washed with acetone to remove any contamination and were dried prior to measuring their contact angle. The removal of PEG conditioning agent was confirmed using ATR-FTIR.

Before BET surface area analysis PEG-400 conditioning agent was removed from the membranes using acetone. The removal of PEG conditioning agent was confirmed using ATR-FTIR. The membranes were dried at room temperature and then degassed overnight at 80 °C to further remove any traces of solvent from the membrane that may interfere with the adsorption of nitrogen onto the membrane surface. The BET surface areas of the membranes were then determined using a gas adsorption analyser (Tristar 3000, Micromeritics, Norcross, GA) which measured the membrane surface area based on nitrogen adsorption.

The surface topographies of the membranes were characterized by tapping-mode atomic force microscopy (AFM) (Innova, Veeco, TESP-SS probes). No alterations were made to the membranes before AFM was performed.

4.2.4 OSN Experimental Procedure

Each membrane (UF, MMM and ISG) was independently prepared two times and two membrane discs were tested from each membrane prepared. The reported results are the mean values of these measurements. All filtration experiments were carried out at 10 bar using a cross-flow filtration system using the same polystyrene/acetone model solution used in chapter 3 (see section 3.2.8 OSN Experimental Procedure). The effective area of each membrane disc was 14 cm². The membranes were tested for 24 hours in order to ensure a steady permeance had been reached. The initial permeance and the final steady state membrane permeance were measured in order to calculate the membrane flux decline. Permeate and retentate solution concentrations were measured using a HPLC. Membrane permeances and rejections were calculated using Equation 2 and Equation 3 respectively.

4.3 Results and Discussion

4.3.1 Preparation of Hybrid Polymer/MOF Membranes

There is a visible colour difference between the ultrafiltration membrane (UF), the mixed matrix membrane (MMM) and the in-situ growth membrane (ISG), this can be seen in the images found in Figure 24. Unprocessed P84 powder is yellow, while HKUST-1 is blue. When HKUST-1 powder is added to the polymer dope solutions for MMM fabrication, the mix of blue and yellow from the HKUST-1 and the P84 respectively produce a green dope solution. The colour of the MMM remains green after the immersion precipitation process, indicating that the HKUST-1 particles remain lodged in the polymer matrix. The yellow P84 membrane turns blue when submerged in the blue HKUST-1
precursor solution during the formation of the ISG membrane. This change in colour is evidence that copper ions have been incorporated within the membrane matrix.

X-Ray Powder Diffraction (XRPD) was carried out on each membrane in order to prove that the colour change that occurs with the ISG membrane is due to the growth of HKUST-1. HKUST-1 is a crystalline material with a regular structure and a well-documented XRPD pattern[183, 192]. The XRPD pattern for pure HKUST-1 is shown in Figure 24, the largest peaks are at 9.3°, 11.4° and 13.1°. The P84 UF membranes are semi-crystalline in structure. The polymer chains are randomly orientated throughout the membrane, and as such the XRPD pattern of the UF membrane is a smooth slope with no clear peaks. The XPRD patterns for both hybrid membranes, MMM and ISG, are a mixture of the features of P84 and the peaks of HKUST-1.

![Figure 24: X-Ray Powder Diffraction (XRPD) data for membranes showing characteristic HKUST-1 peaks blended with the profiles of the P84 UF polymer membrane](image)

Table 5: Thickness, weight per square metre and density of membranes produced in this work.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
<th>Mass (g.m⁻²)</th>
<th>Density (g.cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>102 ± 2</td>
<td>54 ± 2</td>
<td>0.53 ± 0.02</td>
</tr>
<tr>
<td>MMM</td>
<td>99 ± 2</td>
<td>60 ± 3</td>
<td>0.61 ± 0.02</td>
</tr>
<tr>
<td>ISG</td>
<td>107 ± 3</td>
<td>82 ± 2</td>
<td>0.76 ± 0.01</td>
</tr>
</tbody>
</table>

XRPD proved the presence of the HKUST-1 in the membranes but as an analytical method it is only qualitative. In order to obtain quantifiable data about the amount of HKUST-1 in the membranes, the thickness, mass and density of the hybrid membranes were measured and compared with the polymer UF membrane. The masses reported in Table 5 represent the mass of the membrane, minus the weight of the polypropylene backing. Polypropylene was independently submerged in HKUST-1 precursor solution and no significant change in mass was measured.
The difference in thickness between the membranes is negligible. The largest changes can be seen in the weight and the density of the membranes. There is a large increase in weight once HKUST-1 is grown in the ISG membrane, and also a corresponding increase in the density of the membrane. The mass percentage of HKUST-1 in the ISG membrane was estimated based on the increased weight of the membrane using Equation 15.

\[
MOF(\%)_{ISG} = \frac{M_{(ISG)} - M_{(UF)}}{M_{(ISG)}} \times 100 \quad \text{(Equation 15)}
\]

Where the MOF(\%)_{ISG} is the percentage by mass of HKUST-1 in the ISG membrane and \(M_{(ISG)}\) and \(M_{(UF)}\) the mass of the ISG and the UF membrane respectively. Using Equation 15 the MOF(\%) in the ISG membrane is calculated to be 33%. The increase in weight and density of the ISG membrane, along with the negligible change in thickness, indicate that HKUST-1 mostly grows within the pre-existing pores in the UF membrane. The overall porosity of the original UF can be calculated using Equation 16.

\[
\varphi = 1 - \frac{\rho_{(UF)}}{\rho_{(P84)}} \quad \text{(Equation 16)}
\]

Where \(\varphi\) is the porosity and \(\rho_{(UF)}\) and \(\rho_{(P84)}\) are the density of the UF membrane and the P84 polymer respectively. The density of P84 is 1.34 g cm\(^{-3}\) [218], thus the calculated porosity of the UF membrane is 0.6. Using the change in membrane density between the UF and the ISG membrane the extent of pore filling by MOF in the ISG membrane can be calculated using Equation 17.

\[
Pore \ filling \ by \ HKUST \ (\%) = \left[ \frac{(\rho_{(ISG)} - \rho_{(UF)})}{\rho_{(MOF)}} \right] \times 100 \quad \text{(Equation 17)}
\]

Where \(\rho_{(ISG)}\) and \(\rho_{(MOF)}\) are the densities of the ISG membrane and HKUST-1 respectively, and \(\varphi\) is the porosity of the UF membrane. Using a density of 1.22 g cm\(^{-3}\) for HKUST-1 [216], the pore filling by HKUST-1 is 31% based on the additional assumption that no MOF grows outside of the porous structure of the polymer membrane.

The mass of HKUST-1 added to the dope solution for the MMM was at a ratio of 1:5 MOF to polymer, this equates to 17% MOF by weight. The HKUST-1 particles are denser than the surrounding polymer membrane; therefore the percentage of HKUST-1 retained by the membrane can be calculated using the observed increase in density. The percentage mass of HKUST-1 retained by the MMM during the casting process can be calculated using Equation 18.

\[
MOF(\%)_{MMM} = \frac{\rho_{(MMM)} - \rho_{(UF)}}{\rho_{(MOF)} - \rho_{(UF)}} \quad \text{(Equation 18)}
\]

Where MOF(\%)_{MMM} is the percentage by mass of HKUST-1 in the MMM and \(\rho_{(MMM)}\) is the density of the MMM. Using this calculation the mass of HKUST-1 in the MMM amounts to 12%. The observed reduction in MOF(\%) can be attributed to large HKUST-1 particles settling towards the bottom of the dope solution. Excess dope solution is produced to fabricate membranes and therefore the bottom of the dope solution is often not used to produce membranes. As the bottom of the dope solution is
particle rich, the resultant membranes have a lower percentage of MOF than originally added to the
dothe solution.

As a result of its microporous structure, HKUST-1 has a large internal surface area. The BET surface
area of HKUST-1 was measured as 1176 m².g⁻¹, which is in accordance with values found in
literature[198, 199]. The BET surface area of the UF membrane is 10.85 ± 0.02 m².g⁻¹. The BET
surface area of the MMM is 10.17 ± 0.02 m².g⁻¹. The ISG membrane has the highest BET surface
area, 26.1 ± 0.2 m².g⁻¹. The low BET surface areas observed for the hybrid membranes are probably
due to the heating and drying of the membranes required for the BET analysis. This would cause the
collapse of the polymer matrix, sealing the HKUST-1 within the membrane. The BET surface area for
the ISG membrane is higher than for the MMM, indicating that the accessibility of the HKUST-1
micropores is higher in ISG membranes than MMMs.

4.3.2 HKUST-1 Distribution in Hybrid Membranes

The membranes each have the typical structure of integrally skinned asymmetric polymer
membranes formed via phase inversion, with dense top layers, spongy support structures in the
middle of the membrane, and macrovoids at the bottom of the membranes. Figure 25 shows SEM
images from each of the membranes types. Visually there is very little difference between the UF
and ISG membranes. The individual HKUST-1 crystals in the ISG membrane cannot be seen,
suggesting that the crystal sizes must be on the nanometre scale. In the MMM the HKUST-1 crystals
can be clearly seen, as they are on the micron scale. The presence of the HKUST-1 crystals in the
MMM has caused distortion of the macrovoids in the membrane.

Figure 25: SEM images of the cross-section of membranes (top) UF, (middle) MMM and (bottom) ISG

The presence of copper in the membranes was measured using EDX analysis. As HKUST-1 contains
31.5% copper by weight and copper is not found in P84, the copper signal is used to show the
distribution of HKUST-1 in the hybrid membranes. The distribution of copper throughout the cross-
section the hybrid membranes can be found in Figure 26. The heights of the red lines in Figure 26 reflect the relative ‘counts’ of copper throughout the cross-section of the membrane. The presence of copper can be found throughout the cross-section of the ISG membrane at roughly similar values. For the MMM however the copper signal can only be found where the HKUST-1 crystals can be seen. Figure 26 shows that the distribution of HKUST-1 throughout ISG membranes is even and continuous while the distribution of MOF in MMMs is discrete.

![Image of SEM/EDX images of the cross-section of membranes (top) ISG and (bottom) MMM](image)

**Figure 26:** SEM/EDX images of the cross-section of membranes (top) ISG and (bottom) MMM

### 4.3.3 The Surface Properties of Hybrid Polymer/MOF Membranes

Attenuated total reflection Fourier Transform-Infrared (ATR-FTIR) was used to analyse the chemical structure of the surface of the membranes. Figure 27 shows that the ISG membrane IR signal follows the same characteristic peaks as the HKUST-1 powder. The characteristic absorbance at 740, 1380 and 1450 cm\(^{-1}\) are in accordance with those found in literature[219]. The MMM shows no IR evidence of HKUST-1 at the membrane surface, and closely follows the IR signal of the UF membrane. ATR-FTIR can penetrate materials up to 5 microns in depth, so though the HKUST-1 material is located in the MMM, the MOF crystals are not often found at the membrane surface. The lack of HKUST-1 at the membrane surface can be explained by the tendency of the HKUST-1 particles to sink during the membrane casting process. The MOF particles are covered by the polymer dope solution before phase inversion, making siting of HKUST-1 at the membrane surface less favourable.
Copper signals from the surfaces of the hybrid membranes, ISG and MMM, were obtained using SEM/EDX. The presence of copper was used as evidence of the presence of HKUST-1. As in Figure 26, the height of the red lines in Figure 28 reflects the relative ‘counts’ of copper across the surface of the membranes. Figure 28 shows that the surface of the ISG membrane is evenly covered in HKUST-1 crystals, whereas for the MMM there is only a single peak, where a single crystal of HKUST-1 is protruding from the membrane surface. Confirming the data shown in Figure 27 indicating that the surface of the ISG membrane is covered in HKUST-1, whereas for the MMM there is only a single peak where a single crystal of HKUST-1 is protruding from the membrane surface. The SEM/EDX data confirms the data shown in Figure 27, indicating that the surface of the ISG membrane is covered in HKUST-1.
AFM was used to measure changes in the membrane topology caused by the addition of HKUST-1 to polymer membranes. It can be seen in Figure 29 that the surface of the UF membrane is mostly flat and featureless. The surface of the MMM is also mostly flat, though it has large defects in the surface, caused by the disruption of the membrane by HKUST-1 particles in the membrane formation process. This confirms the ATR-FTIR and EDX data for the MMM. The surface of the MMM remains mostly P84, but the topology has been changed due to the presence of MOF particles below the membrane surface. The most comprehensive change to the membrane surface is observed in the ISG membrane. The flat surface of the UF membrane has completely changed in topology. The HKUST-1 has grown across the surface of the membrane, introducing large features, up to 100 nm in height, across the membrane surface. HKUST-1 covers the top layer of the ISG membrane, which...
indicates that the MOF should have a larger influence on the selective properties of the ISG membrane than the MMM, whose surface remains largely polymer.

The water contact angle of the UF membrane was measured as 62±1°, proving that the membrane is fairly hydrophilic in nature. The contact angles for both the hybrid HKUST-1 membranes, MMM and ISG, were 58±4° and 65±2° respectively. The addition of HKUST-1 appears to have little influence on the hydrophillicity of P84 UF membranes.

### 4.3.4 Membrane Performance

The permeance data from the two hybrid membranes (MMM and ISG) and the polymer support membrane (UF) are reported in Table 6. The UF membrane has the highest flux (177 L m⁻² h⁻¹ bar⁻¹) and the highest flux decline (18%). Polymer nanofiltration membranes (Molecular weight cut-off (MWCO) ≈ 1700 g mol⁻¹) in the same experimental set-up had an initial permeance of 5.6 L m⁻² h⁻¹ bar⁻¹ and a flux decline of 31%, showing, that even with a low initial permeance, flux decline is still an issue for integrally skinned asymmetric polymer membranes. The MMM had the second highest permeance, and a lower flux decline than the polymeric membranes. The ISG membranes had the lowest flux decline of all the membranes tested with a value of 2%. The 9 times reduction in flux decline observed in ISG membrane compared to the UF membrane is probably due to the additional rigidity of the HKUST-1 resisting the effects of compaction. In the case of the ISG membrane the HKUST-1 fills the pores in the polymer matrix; this impedes the rearrangement of the polymer chains on a microscopic scale, leading to negligible flux decline. The flux decline of the MMM is slightly larger than that of the ISG membrane. Here any reduction in flux decline is probably due to the macroscopic mechanical properties of the membrane. The large HKUST-1 crystals in the MMM act as a rigid support to the whole membrane structure, reducing the compression of the membrane by the applied pressure, though polymer chains can still rearrange on a microscopic scale.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Initial Acetone Permeance (L m⁻² h⁻¹ bar⁻¹)</th>
<th>Final Acetone Permeance (L m⁻² h⁻¹ bar⁻¹)</th>
<th>Flux Decline</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>217 ± 1.8</td>
<td>177 ± 14</td>
<td>18%</td>
</tr>
<tr>
<td>MMM</td>
<td>99.0 ± 30</td>
<td>93.2 ± 32</td>
<td>6%</td>
</tr>
<tr>
<td>ISG</td>
<td>18.4 ± 4.2</td>
<td>18.0 ±3.6</td>
<td>2%</td>
</tr>
</tbody>
</table>

The rejection performances of the membranes can be found in Figure 30. The UF membrane has a very flat profile with the lowest rejections. Both the ISG and MMM have higher rejections than the UF membrane, with the highest rejections achieved by the ISG membrane.

In this chapter MMMs were shown to outperform polymer UF membranes, whereas in the previous chapter MMMs show no discernable improvement on the performances of polymer membranes. Both chapters show that HKUST-1 particles are not found near the surface of MMMs, therefore any difference in performances between MMMs and polymer membranes must be due to changes in the configuration of the polymer itself. SEM images and AFM show that the addition of MOFs alter the morphology of polymer membranes, these morphological differences are due to the influence of the
MOF particles in the phase inversion process. For UF membrane dope solutions, these changes lead to a slight tightening of the membrane, leading to higher solute retentions and lower permeances. For dope solutions containing a mixture of DMF and Dioxane the phase inversion conditions already lead to the formation of tight membranes, therefore any tightening effect the MOFs may have are negligible.

It can be seen in Figure 30 that the error bars on the rejection curves of MMM are significantly larger than the error bars of the UF and ISG membranes. This can be attributed to the structural nature of the MMMs. The structure of the MMMs is naturally less homogenous than the polymer membranes and the ISG membranes due to their fabrication methodology. The random dispersion of discrete HKUST-1 particles in the membranes causes some areas of the membrane sheet MOF rich, while other areas are low in MOF. This could lead to membranes coupons having differing membrane performances, which could explain the size of the MMM error bars.

![Figure 30: MWCO curves for P84 membranes (UF), mixed matrix membranes (MMM) and in-situ growth MOF membranes (ISG) tested at 10 bar with polystyrene in acetone solvent. Mean data for each membrane plotted, error bars show one standard deviation](image)

Table 7: Calculated rejections for the membranes in the nanofiltration range at low MW ($R_{250}$), mid-range MW ($R_{750}$) and high MW ($R_{1500}$)

<table>
<thead>
<tr>
<th>MW</th>
<th>UF (%)</th>
<th>MMM (%)</th>
<th>ISG (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{250}$</td>
<td>8.1</td>
<td>14.4</td>
<td>13.4</td>
</tr>
<tr>
<td>$R_{750}$</td>
<td>15.9</td>
<td>32.0</td>
<td>42.7</td>
</tr>
<tr>
<td>$R_{1500}$</td>
<td>16.2</td>
<td>41.5</td>
<td>62.4</td>
</tr>
</tbody>
</table>
Further analysis of the polystyrene rejection curves can be found in Table 7. Rejections of the polystyrene markers were calculated for low range molecular weight (MW) solutes, 250 g mol\(^{-1}\), mid-range MW solutes, 750 g mol\(^{-1}\), and high MW solutes, 1500 g mol\(^{-1}\).

The rejection and permeance data suggests that the addition of HKUST-1 to polymer UF membranes via both in-situ growth and dispersion of ex-situ grown crystals in the polymer dope changes the transport properties of the membranes.

The rejection and permeance performance of the ISG membrane would appear to confirm that HKUST-1 growth occurs within the pre-formed porous structure of the UF membrane. HKUST-1 has a pore-filling effect on ISG membranes, slowing solvent transport, and reducing the average pore size of the selective layer of the membranes. The improved solute retention performance of the ISG membranes over the MMM could be due to the more continuous nature of the membranes. SEM/EDX and AFM analyses showed that the MOF phase in the ISG membranes is more evenly spread in ISG membranes. BET analysis showed that the HKUST-1 pores were more accessible in the ISG membranes than in MMMs. However it can be surmised that perfect MOF coverage throughout the hybrid membrane has not been achieved using ISG fabrication as the small pore size of the HKUST-1, 0.9 nm, should retain all but the smallest polystyrene oligomers.

4.3.5 Pressure Driven Membrane Compaction and Flux Decline

In order to test the effect of pressure on compaction and flux decline on filtration tests were carried out at different applied pressures, 6 bar and 27 bar. In addition to crosslinked polymer membranes (UF), other polymer membranes, non-crosslinked membranes (UF-NC), and crosslinked polymer membranes produced from DMSO solvent (UF-DMSO) were tested and compared to the ISG membrane.

The UF-NC membrane was chosen to observe the flux decline of a non-crosslinked polymer membrane. Crosslinking may restrict the movement of the polymer chains, leading to less rearrangement of the polymer chains on a microscopic scale. The UF-DMSO membrane was chosen in order to test whether macrovoid collapse significantly contributed to flux decline. Casting P84 membranes from DMSO solvent systems leads to the formation of macrovoid free sponge-like membranes[113]. Macrovoids, large polymer free areas, usually found at the bottom of polymer membranes form in the latter stages of the phase inversion process, and can collapse under pressure, reducing the porosity of polymer membranes. Casting P84 from DMSO hinders the latter stages of the phase inversion process, reducing macrovoid formation.

Two different pressures, 6 bar and 27 bar, were used to test the effect of applied pressure on flux decline and physical compaction. These pressures are set above and below the previously used pressure of 10 bar and are close to commonly used pressures in ultrafiltration processes (6 bar) and nanofiltration processes (27 bar) respectively. The physical effects of the applied pressure were also accounted for by measuring the change in thickness of the membranes before and after filtration.

Table 8 shows the permeance of the polystyrene solutions and the corresponding flux declines. The flux decline of the ISG membrane is lower than both the UF and UF-NC membranes, but higher than the UF-DMSO membrane.
**Table 8**: Permeance of 1 g L$^{-1}$ polystyrene solution in acetone at 6 bar applied pressure through the membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Initial Acetone Permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>Final Acetone Permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>Flux Decline</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>96 ± 3.0</td>
<td>81 ± 0.0</td>
<td>16%</td>
</tr>
<tr>
<td>UF-DMSO</td>
<td>158 ± 6.1</td>
<td>150 ± 6.1</td>
<td>5%</td>
</tr>
<tr>
<td>UF-NC</td>
<td>171 ± 36</td>
<td>124 ± 18</td>
<td>28%</td>
</tr>
<tr>
<td>ISG</td>
<td>7.6 ± 1.3</td>
<td>6.1 ± 1.7</td>
<td>13%</td>
</tr>
</tbody>
</table>

**Figure 31** shows the rejection of these membranes at 6 bar applied pressure. The ISG membrane has a higher rejection than the polymer membranes (UF, UF-DMSO and UF-NC) at this pressure, with the UF-DMSO membrane displaying the lowest rejection.

**Figure 31**: MWCO curves for crosslinked P84 membranes (UF), crosslinked P84 membranes made from DMSO solvent (UF-DMSO), non-crosslinked P84 membranes (UF-NC) and in-situ growth MOF membranes (ISG) tested at 6 bar with polystyrene in acetone solvent. Mean data for each membrane plotted, error bars show one standard deviation.
Table 9: Permeance of membranes at 27 Bar applied pressure

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Initial Acetone Permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>Final Acetone Permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>Flux Decline</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>78</td>
<td>48</td>
<td>39%</td>
</tr>
<tr>
<td>UF-DMSO</td>
<td>141</td>
<td>105</td>
<td>26%</td>
</tr>
<tr>
<td>UF-NC</td>
<td>110</td>
<td>70</td>
<td>36%</td>
</tr>
<tr>
<td>ISG</td>
<td>8.6</td>
<td>6.6</td>
<td>22%</td>
</tr>
</tbody>
</table>

The permeance data for the membranes at 27 bar can be found in Table 9, these membranes were tested at 27 bar with a single membrane disc. At 27 bar the measured flux decline is higher than the flux decline measured at 6 bar for each membrane. The final and initial permeances of the polymer membranes (UF, UF-DMSO and UF-NC) are significantly lower at 27 bar than at 6 bar, showing that for polymer membranes increased pressure has an adverse effect on permeance through the membrane. The ISG membrane has the lowest flux decline at 27 bar. The UF-DMSO membrane, which previously had the lowest flux decline, has a much higher flux decline at 27 bar.

Figure 32: MWCO curves for single discs of crosslinked P84 membranes (UF), crosslinked P84 membranes made from DMSO solvent (UF-DMSO), non-crosslinked P84 membranes (UF-NC) and in-situ growth MOF membranes (ISG) tested at 6 bar and 27 bar with polystyrene in acetone solvent.
**Figure 32** shows the rejection of the membranes at both 6 and 27 bar applied pressure. For the UF and UF-NC membranes there was an increase in rejection from 6 to 27 bar, for the UF-DMSO membrane the rejection decreased, while for the ISG membrane the rejection remained constant.

**Figure 33** shows the relationship between flux decline and the decrease in membrane thickness at both 6 bar and 27 bar for each of the membranes. For each of the polymer membranes the thickness decrease and flux decline increased with increased pressure. The general trend for the all of the membranes is that larger flux declines are associated with large decreases in membrane thickness. For the ISG membrane the thickness decrease and flux decline is similar for membranes used in 6 bar and 27 bar processes.

**Figure 33**: Reduction of membrane thickness with corresponding reduction in membrane flux for single discs at given pressures.

**Figure 33** shows that the uncrosslinked UF-NC has significant thickness decreases at both applied pressures, showing that crosslinking the membranes aids in the physical strengthening of polymer
membranes, and thus reduces flux decline. The UF-DMSO membrane has very low flux decline and thickness decrease at low pressure (6 bar), but rises to levels comparable to the ISG membrane at higher pressure (27 bar). The thickness change and flux decline data for the UF-DMSO membrane, along with the reduction in rejection, may suggest that the limit of pressurisation for the membrane may be fairly low. At 27 bar the membrane performance significantly worsens and the thickness decreases by over 25%.

Figure 34 and Figure 35 show the morphology of the UF and the UF-DMSO membrane respectively before and after testing at both pressures. The UF membrane, formed from DMF, contains macrovoids, which are shown to collapse at both pressures after testing. The UF-DMSO membrane contains no macrovoids, as predicted, and shows no significant changes in membrane morphology before and after testing, though the membrane thickness can be seen to decrease.

Figure 34: UF membrane (left) before testing, (middle) after testing at 6 bar and (right) after testing at 27 bar

Figure 35: UF-DMSO membrane (left) before testing, (middle) after testing at 6 bar and (right) after testing at 27 bar

Figure 36: UF-NC membrane (left) before testing, (middle) after testing at 6 bar and (right) after testing at 27 bar
Figures 36 and 37 show the morphology of the UF-NC and ISG membranes before and after testing. Before testing, the UF-NC membrane contains macrovoids, as it is formed from a DMF solution. The macrovoids are shown to collapse after testing at 6 and 27 bar. In addition to the collapse of the macrovoids, the membrane morphology significantly changes after testing, the membrane thickness has significantly decreased and the membrane looks significantly denser. Figure 37 shows the morphological changes of the ISG membrane before and after testing. The macrovoids in the ISG membranes collapse as with the polymer membranes. The flux decline, and thickness change measurements indicate that the MOF within the ISG membrane helps reduce the compaction of the hybrid membrane, though not significantly enough to stop the macrovoids from collapsing.

This study on the effects of pressure on membranes, both morphologically and performance wise confirms that ISG MOF aides in the reduction of pressure driven compaction effects which in turn leads to a reduction in flux decline. Producing membranes without macrovoids can also reduce flux decline though there is a pressure threshold for these membrane, after which the membrane performance worsens, both for permeance and solute retention.

4.4 Conclusions

This chapter compares and contrasts two hybrid polymer/MOF membrane fabrication methodologies, the mixed matrix membrane (MMM) approach and *in-situ* growth (ISG) of MOFs in pre-existing polymer membrane pores. The analytical methods used to characterise the structure of the hybrid membranes, along with the OSN performance data, indicate that ISG membranes have several advantages over MMMs. These advantages include, an even spread of HKUST-1 throughout the cross-section and across the surface of the ISG membranes, proved by EDX and AFM, higher accessibility to the HKUST-1 pores, proved by BET analysis and reduced flux decline. The ISG hybrid membrane fabrication approach could be used in the future to produce gas separation membranes and membranes used for combined catalysis and separation processes.

Though the ISG fabrication approach showed improved performances above that of MMMs and polymer membranes the rejection and permeance performances of the membranes could be further improved. This could be achieved in a number of ways including the incorporation of chemical modification agents to improve the adhesion between the polymer and the MOF phases, leading to improved solute retentions. Also the development of ISG membranes containing MOFs other than HKUST-1 could be used to exert more control on the membrane rejections. The use of MOFs with different pore sizes would allow for control of the molecular weight cut-offs of ISG membranes based purely on the pore size of the chosen MOF. Methodologies to improve the performance of
ISG membranes are explored in Chapter 5. The permeance performance of hybrid polymer/MOF membranes could be improved by reducing the thickness of the MOF selective layer. This could be achieved by utilising interfacial synthesis to produce MOF thin films. The study of MOF thin films, formed via interfacial synthesis can be found in Chapter 6.
Chapter 5

5. Improving the Performance of In-Situ Growth Hybrid Polymer/Metal Organic Framework Membranes

5.1 Introduction

Chapter 4 introduces and details the design and fabrication of hybrid polymer/metal organic framework (MOF) membranes known as in-situ growth (ISG) membranes. These membranes are shown to perform favourably compared to polymer membranes in both solute retentions and membrane flux decline. ISG membranes were also shown to outperform mixed matrix membranes (MMMs) in these aspects as well. However ISG membranes display low permeances, while solute retentions could also be improved upon. This chapter describes a number of methodologies which have been utilised to improve the performances of ISG hybrid polymer/MOF membranes and further explore the fabrication of these membranes.

5.1.1 A Study of the Parameters Controlling the Growth of HKUST-1 within Polymer Membranes

A number of parameters can be used to control the rate and extent of the HKUST-1 reaction, including reaction solution concentration, temperature and time. Varying these three properties could lead to improving the growth of HKUST-1 in ISG membranes and thus improving the rejection performances of ISG membranes.

By altering the concentration of the reagents the rate of MOF formation can be altered. A slow rate of reaction may allow the reagents to diffuse into the polymer membrane interior before reacting, leading to improved coverage. However decreasing the concentration of the reagents may mean not enough MOF material is available to fill the pores of the polymer support. Alterations to the concentration of the reagents were made to test whether any gains in HKUST-1 coverage could be made.

While HKUST-1 can be fabricated at room temperature[220], most HKUST-1 fabrication methodologies suggest synthesis at temperatures above 70 °C [160, 212]. Increasing the temperature of reaction could lead to increased MOF growth and improved coverage, leading to less defects and improved solute retentions. High temperature synthesis (70 °C) of ISG membranes was attempted using polyimide P84 membranes, as well as membranes produced from the polymers PEEK and PBI.

As HKUST-1 formation is a time dependent reaction the extent of membrane exposure to the reaction mixture could influence the amount of MOF growth within ISG membranes. The effect of time on MOF growth was tested to find how long it takes for the ISG fabrication process to complete. Alongside the time effects, the exposure of the separate reagents to P84 was measured to ensure that any growth measured was due to the growth of MOF within the membranes.

5.1.2 Fabrication of Hybrid Polymer/MOF membranes on Dense Polymer Supports

Another route to improve the performance of the hybrid polymer/MOF ISG membranes is to alter the nature of the polymer support membranes used to produce these membranes. Both MMMs and ISG membranes were fabricated using dense polymer membranes. Dense polymer membranes have
less porous structures, leading to higher solute retentions. By improving the performance of the base UF membrane to that of a dense support membrane, UF(D), the overall performance of the hybrid membranes could also be improved.

5.1.3 Chemical Modification as a Tool to Improve the Performance of In-Situ Growth (ISG) Membranes

The performance of ISG membranes could be improved by modifying the chemical nature 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[146, 221] and OSN[70, 71]. The use of crosslinking molecules to improve the adhesion between polyimide and HKUST-1 is also discussed in Chapter 3.

Post-polymerization chemical modification can be used to incorporate functionalities into existing polymer chains. 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. In order to achieve improved solute rejections using ISG membranes, chemical modification agents are used with a view to reducing the defects between polymer and the MOF crystals. In this chapter chemical modification has been applied to encourage growth of the MOF (HKUST-1) directly on the walls of the pores, reducing voids between the polymer and MOF crystals. This is achieved through the incorporation of benzene tri-carboxylate functional groups into the polyimide polymer chain. The addition of this functional group should promote HKUST-1 crystal growth via coordination of copper ions directly onto the polymer surface.

5.1.4 Chapter Aims

This chapter aims to explore three routes to improve the solute retentions of ISG membranes into the nanofiltration range. Firstly the parameters of HKUST-1 formation will be studied to find suitable conditions for the fabrication of ISG membranes. Secondly the morphology and density of the polymer support membranes used are altered, using dense polymer supports to improve solute retentions. Finally the chemical modification of the polymer support membranes will be carried out to improve the adhesion between the polymer and MOF phases of the ISG membranes and thus improve solute retentions. The rejection of the best performing membranes will be compared to the predicted rejections of HKUST-1 membranes using the Bowen and Welfoot pore flow membrane model.

5.2 Experimental

5.2.1 Materials

The materials used in this chapter are identical to those used in Chapters 3 & 4 (see section 3.2.1 Materials). With the addition of 1,2,4-Benzeneetricarboxylic anhydride, used as a chemical modification agent (CMA), purchased from Sigma-Aldrich.

5.2.2 Membrane Preparation

Polymer ultrafiltration (UF) membranes were produced as described in Chapter 4 (See section 4.2.2 Membrane Preparation). Dense polymer ultrafiltration membranes (UF(D)) were fabricated using
the same dope solution composition, and the same preparation methodology. However the membranes were cast in an environment with a temperature of 15 °C and a humidity of 50-60%.

Dope solutions used to produce dense MMMs (MMM(D)) were prepared using the same procedure used to produce MMMs as described in Chapter 4 (see section 4.2.2 Membrane Preparation). As with the UF(D) membranes the MMM(D) membranes were cast in an environment with a temperature of 15 °C and a humidity of 50-60%.

Crosslinked Polybenzimidazole (PBI) membranes were fabricated following the procedure described by Valtcheva et al.[118]. Polyeher ether ketone (PEEK) membranes were fabricated following the procedure described by Burgal et al. [222], except the membranes were not dried.

Dense in-situ growth (ISG(D)) membranes were fabricated using dense polymer UF(D) membranes as structural scaffolds. HKUST-1 growth in ISG(D) membranes was carried out using copper nitrate and 1,3,5-benzenetricarboxylic anhydride in DMF:ethanol solutions (ratio 60:40), at the same concentrations as used in Chapter 4 (see section 4.2.2 Membrane Preparation). Membrane conditioning was carried out by submerging the membranes in a PEG400:IPA (60:40 v/v) solution for 12 hours.

**Figure 38:** (Top) Polyimide P84 crosslinking reaction with hexane-1,6-diamine (HDA)[63], the opening of the imide ring leaves the polymer structure with four secondary amide units per monomer unit available to react with the CMA 1,2,4-benzenetricarboxylic anhydride. (Bottom) Schematic representation of the introduction of a BTC moiety to the membrane surface in order to provide a chemical anchor for HKUST-1 growth.
Prior to chemical modification UF(D) membranes were washed with DMF in order to remove IPA from the pores. The membranes were placed in a solution of CMA, 1,2,4-benzenetricarboxylic anhydride, in DMF and the mixture was stirred for 20 hours. The amount of CMA was based on the assumption that each polymer unit contains four sites available to react with the 1,2,4-benzenetricarboxylic anhydride (see Figure 38). For each membrane one equivalent of CMA was added using a 10 g L\(^{-1}\) solution of 1,2,4-benzenetricarboxylic anhydride in DMF. After the reaction each membrane was excessively washed with DMF to remove any unreacted CMA from the polymer matrix.

5.2.3 Membrane Characterisation

Membrane characterisation was carried out using the following methodologies, mass, density and thickness measurements, ATR-FTIR, SEM/EDX and XRPD. Each methodology was carried out as stated in Chapter 4 (see section 4.2.3 Membrane Characterisation).

5.2.4 Testing the Effect of Temperature on ISG Membrane Fabrication

In order to test the effect of temperature on ISG membrane fabrication polymer membranes were submerged in a HKUST-1 reaction solution of copper nitrate and benzene tricarboxylic acid in DMF at 70°C for 12 hours. The polymer membranes selected were ultrafiltration polyimide P84 membranes (UF), Polyether ether ketone (PEEK) membranes and polybenzimidazole (PBI) membranes.

5.2.5 Testing the Effect of Time on ISG Membrane Fabrication

The growth of HKUST-1 over time within P84 UF membranes was investigated using 3x3 cm squares of UF and ISG membrane, fabricated as stated in section 5.2.2. However before the membranes were conditioned using PEG400:IPA preserving agent the membranes were washed with IPA and acetone to remove excess reagents, and then dried. The growth of HKUST-1 was monitored by measuring the increase of mass with time. The mass of each membrane sample was measured using an electronic scale.

5.2.6 OSN Experimental Procedure

PBI and PBI-ISG membranes were test in a dead end cell, using single discs of each membrane. All other membranes were tested in cross-flow filtration set-up, using at least 2 separate discs from separate membrane sheets. All membrane tests were carried out using polystyrene model solutions in either acetone or DMF solutions. Membrane permeances and solute rejections were obtained and calculated using the same procedure as described in in Chapter 3 (see section 3.2.8 OSN Experimental Procedure).

5.3 Results and Discussion

5.3.1 A Study of the parameters controlling the growth of HKUST-1 within Polymer Membranes

The reagent concentration chosen to grow HKUST-1 in ISG membranes was selected to maximise the amount of reagents available to fill the pores of the UF membrane. At concentrations over 50 g L\(^{-1}\) in a 60:40 mixture of DMF/ethanol benzene tricarboxylic acid quickly precipitated. The 83.3 g L\(^{-1}\) concentration of copper nitrate in the reaction mixture was chosen in order to keep the reagents close to stoichiometric ratios. The concentrations of the HKUST-1 reagents were halved to 25 g L\(^{-1}\).
for benzene tricarboxylic acid and 41.7 g L\(^{-1}\) for copper nitrite in order to test the effects of concentration on the formation of the ISG membranes.

High HKUST-1 concentrations could lead to rapid reaction rates. If the reaction rate exceeds the rate of diffusion of the reagents then the bulk of MOF formation could occur outside of the membrane matrix. The concentrations of the benzene tricarboxylic acid and copper nitrate were reduced with a view to testing whether using the maximum possible reagent concentrations leads to better membranes.

**Figure 39** shows the effect of reducing the solution concentration on the membrane visually. It can be seen in **Figure 39** that the original solution concentration at the limits of benzene tricarboxylic acid solubility produces membranes with a rich blue colour, which is consistent and even across the membrane surface. Whereas the membrane produced at half the concentration was shown to be lighter in colour and with more visible defects.

**Figure 39**: (left) ISG membrane produced at the original reagent concentrations (right) ISG membrane produced at half the original reagent concentration

ISG membranes have previously been produced at room temperature, as demonstrated in Chapter 4. Synthesis of HKUST-1 usually occurs at elevated temperature; therefore increasing the reaction temperature could increase the rate of reaction forming HKUST-1 within the membranes. P84 UF membranes were submerged in ISG reaction mixtures at 70°C. When the membrane was removed from solution the P84 had been completely destroyed leaving only the polypropylene non-woven backing. Crosslinked UF membranes were found to be stable in DMF and ethanol at 70°C, BTC solution at 70°C and Cu(NO\(_3\))\(_2\) solution 70°C. When the test was repeated at an intermediate temperature (50 °C) the membrane was also dissolved by the solution. While polyimide P84 has high solvent resistance it has low stability in acidic conditions\[^{118}\].

\[
3 \text{Cu(NO}_3\text{)}_2 + 2 \text{H}_3\text{(BTC)} \rightarrow \text{Cu}_3\text{(BTC)}_2 + 6 \text{HNO}_3 \quad \text{(Equation 19)}
\]

As is shown in **Equation 19**, the MOF formation reaction forms nitric acid. Nitric Acid, pK\(_a\) = 3.12 – 4.70\[^{223}\], is a much stronger acid than benzene tricarboxylic acid, pK\(_a\) = -1.38\[^{224}\], and more readily disassociates protons. The increased acidic conditions could be causing the membrane to disintegrate. The raised temperature causes an increase in the rate of reaction and thus the amount
of nitric acid in the solution. Therefore fabricating ISG membranes at elevated temperatures may require the use of membranes which are stable in acidic conditions and high temperatures. Two possible options for polymers to produce acid stable membranes are Poly Ether Ether Ketone (PEEK) and polybenzimidazole (PBI). Both PEEK and PBI have been demonstrated to be stable in acidic conditions\cite{118, 222}. Using membranes laboratory fabricated membranes both polymers were submerged in HKUST-1 reaction mixtures at high temperature in order to test both the pH-stability and the adhesion of HKUST-1 to the polymers.

![Figure 40: PEEK Membrane treated in HKUST-1 at high temperature](image)

Figure 40 shows that HKUST-1 can grow on the surface of PEEK membranes, but adhesion was poor. The HKUST-1 easily cracked and flaked from the membrane surface thus making the membrane unsuitable for testing.

After treatment in the HKUST-1 reaction mixture the PBI membrane turned from a brown to green. This colour change is shown in Figure 41.

![Figure 41: PBI before treatment (left) and after treatment (ISG-PBI) (right)](image)
The rejection data of the original (PBI) and treated (ISG-PBI) membrane is shown in **Figure 42**. While the permeance values for these membranes can be found in **Table 10**. Adding HKUST-1 to the PBI membrane had a negative effect on the retention of solutes achieved by the membrane. However the permeance values achieved were significantly improved. This is in contrast to the results achieved using P84 membranes and HKUST-1 where addition of the MOF reduced the flux of the membranes. However these results were obtained using only single membrane discs, in a dead-end filtration cell set-up and therefore may not be indicative of the possibilities achievable using ISG-PBI membranes.

**Figure 42**: Rejection of polystyrene markers in DMF in a dead-end filtration cell at 15 bar applied pressure

**Table 10**: Permeance Data of a polystyrene/DMF solution in a dead-end filtration cell at 15 bar applied pressure for PBI and ISG-PBI membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeance (L m⁻² h⁻¹ bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBI</td>
<td>0.2</td>
</tr>
<tr>
<td>ISG-PBI</td>
<td>6.5</td>
</tr>
</tbody>
</table>

The relationship between HKUST-1 growth and time was measured by recording the changing mass of ISG membranes over time. The growth of HKUST-1 in P84 UF membranes was recorded as the change in the observed mass of the membranes per unit of surface area. **Figure 43** shows that the mass of the ISG membrane rapidly increases after the first hour of exposure to the reaction mixture.
More than 60% of the MOF growth within the membranes occurs in the first hour of reaction. HKUST-1 growth continues for around 24 hours after which the measured weight increase begins to plateau.

![Figure 43: Increase mass of ISG membranes with given time in the reaction mixture](image)

The membranes were also left in solutions containing the individual reagents benzene tricarboxylic acid (BTC) and copper nitrate (Cu) to see if the reagents alone could be causing the change in mass. It was found that both the reagents caused a slight mass increase in membrane mass after 24 hours of exposure. Though adding both of these masses together (14.2 g per m$^2$) is less than half of the increase in mass recorded for the ISG membrane at 24 hours (37.4 g per m$^2$).

### 5.3.2 Fabrication of Hybrid Polymer/MOF membranes on Dense Polymer Supports

In order to improve the performance of the hybrid polymer/MOF membranes, both the MMM and ISG membrane fabrication methodologies were tested using dense polymer membrane supports. Dense membranes have slightly less porous structures leading to higher solute retentions. By improving the performance of the base UF membrane to that of a dense support membrane, UF(D), the overall performance of the hybrid membranes could also be improved.

The thickness, mass and density of the dense polymer support membrane, UF(D) and the subsequent hybrid membranes, MMM(D) and ISG(D) are reported in Table 11. The dense membranes are 30 to 40 µm thinner than the original membranes (data can be found in Chapter 4). The ISG(D) membrane has a calculated HKUST-1 weight percentage of 32%, which is similar to that observed in the original ISG membrane. The UF(D) has a calculated porosity of 0.52, making it less...
porous than the original UF membrane. The calculated pore filling of the ISG(D) membrane is 52%, compared to 31% with the original ISG membrane.

**Table 11**: Thickness, mass per square metre, density and surface area of the denser membranes used in this study

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
<th>Mass (g.m²)</th>
<th>Density (g.cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF(D)</td>
<td>67 ± 1</td>
<td>43 ± 3</td>
<td>0.64 ± 0.05</td>
</tr>
<tr>
<td>MMM(D)</td>
<td>70 ± 5</td>
<td>47 ± 6</td>
<td>0.67 ± 0.09</td>
</tr>
<tr>
<td>ISG(D)</td>
<td>65 ± 3</td>
<td>63 ± 2</td>
<td>0.97 ± 0.06</td>
</tr>
</tbody>
</table>

**Figure 44**: (Top row) SEM images of the cross-section of membranes (A) UF(D), (B) ISG(D) and (C) MMM(D), (Bottom row) further close ups of the cross-sections of the (A) UF(D) and (B) ISG(D) membranes

SEM images of the dense membranes are shown in Figure 44. The membranes appear to have shorter, broader macrovoids than the original membranes and a larger spongy support layer in the middle of the membrane. The ISG(D) membrane looks visibly different from the UF(D) membrane. The growth of HKUST-1 in the dense polymer support membrane causes large parts of the cross-section of the membrane to become smooth in appearance. This effect is shown more clearly by the SEM images of the top layer of the UF(D) and ISG(D) membranes, images D and E respectively, in Figure 44. The top of the UF(D) membrane has a porous structure consisting of nodules of polymer. The nodular structure of polymer has completely disappeared from the top of the ISG(D) membrane. The difference in the UF(D) density, porosity and structure make the effect of pore filling by the MOF more obvious.
The rejection and permeance data for the dense membranes follows the same trends as original UF, MMM and ISG membranes. The permeance data for the dense membranes can be found in Table 12, and the rejection data can be found in Figure 45.

**Table 12**: Pure solvent flux of membranes with calculated flux decline in acetone at 10 bar

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Initial Acetone Permeance (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
<th>Final Acetone Permeance (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
<th>Flux Decline</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF (D)</td>
<td>215 ± 49</td>
<td>120 ± 40</td>
<td>44%</td>
</tr>
<tr>
<td>MMM (D)</td>
<td>70.7 ± 4.5</td>
<td>61.7 ± 2.1</td>
<td>13%</td>
</tr>
<tr>
<td>ISG (D)</td>
<td>15.4 ± 2.1</td>
<td>15.1 ± 2.7</td>
<td>2%</td>
</tr>
</tbody>
</table>

**Figure 45**: MWCO curves for P84 membranes (UF(D)), In-situ growth MOF membranes (ISG(D)) and mixed matrix membranes (MMM) tested at 10 bar with polystyrene in acetone solvent. Mean data for each membrane plotted, error bars show one standard deviation.

The increased density of the UF(D) membrane leads to higher rejections of the polystyrene oligomers and a decrease in the final acetone permeance. Flux decline remains an issue with the UF(D), indicating that even dense polymer supports suffer compaction and flux decline. In fact the dense membrane suffers from even higher flux decline than the original UF membrane. The permeance of the MMM(D) is, 61.7 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), which is lower than the original MMM. The MMM(D) has a flux decline of 13%, twice as large as the original MMM, though the flux decline is
still less than both the UF and the UF(D). The ISG(D) has the highest rejection of all the membranes, and permeance and flux decline values of 15.1 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ and 2% respectively.

The decreases in permeance for the dense membranes compared to the original membranes are 32% for the UF membranes, 33% for the MMMs and 16% for the ISG membranes. The decrease in permeance can be explained by the reduced porosity of the polymer membranes.

Experiments to control the solute retentions of UF polymer membranes showed that both the flux and solute retentions of the membranes were highly variable. The phase inversion process is affected by a number of variables, and the influence of temperature and humidity on the formation of P84 ultrafiltration membranes is not documented. When analysing the results of hybrid membranes, it is always important to make like for like comparisons, considering the effect of the base polymer membrane, as this may have a large influence on the results obtained.

5.3.3 Chemical Modification as a Tool to Improve the Performance of Hybrid Polymer/MOF In-Situ Growth Membranes

Chemical modification was performed on UF(D) 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 forming a carboxylate functional group available to react with copper ions to begin forming the building blocks of HKUST-1 within the membrane.

The ATR-FTIR spectra (Figure 46) confirms that the CMA has been grafted successfully onto the surfaces of the membranes UF(D)-CMA and ISG(D)-CMA. The broad peak between 2400 and 2700 cm$^{-1}$ is demonstrative of the stretching of the carboxylic acid O-H bond in membranes UF(D)-CMA and ISG(D)-CMA, caused by the presence of the CMA in the membrane matrix. The characteristic peaks at 740, 1380 and 1450 cm$^{-1}$ confirms the presence of HKUST-1[219] in the ISG(D) and ISG(D)-CMA membranes.

Figure 46: Chemical modification and MOF growth via ATR-FTIR spectra of the prepared polyimide membranes, the inset graph shows the broad peak associated with the addition of 1,2,4-benzenetricarboxylic anhydride to the membrane structure.
The permeance data, found in Figure 47, indicates that addition of the CMA has a slight tightening effect on the polymer. The permeance of the UF(D) membrane was 120 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) at steady state while the permeance of the UF(D)-CMA membrane is lower at 80 L m\(^{-2}\) h\(^{-1}\) at steady state.

The permeance values of the MOF membranes, ISG(D) and ISG(D)-CMA, indicate pore filling has occurred and reduced solvent flow through the membrane pores. The permeability of the ISG(D) membrane was 15 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) at steady state, an almost tenfold reduction in permeability compared to the permeability of UF(D) indicating a large amount of pore blocking in this membrane. The permeability of ISG(D)-CMA is 66 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) compared to 80 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) for the UF(D)-CMA membrane.

Figure 47: Pure acetone over time for P84 membranes (UF(D)), surface modified P84 membranes (UF(D)-CMA) and MOF modified membranes (ISG(D), ISG(D)-CMA). Mean data for each membrane plotted, error bars show one standard deviation.

The addition of HKUST-1 to P84 ultrafiltration membranes is intended to modify the pores sufficiently so as to increase the membrane molecular weight cut-off (MWCO) into the nanofiltration range (200 – 1000 g mol\(^{-1}\)). Figure 48 shows the average MWCOs of each of membrane tested. The addition of the CMA to the UF(D)-CMA membrane slightly increases the rejection of polystyrene markers as compared to the polystyrene rejection of the plain P84 membrane, UF(D). As expected the addition of HKUST-1 to the P84 membranes increased the rejection of the polystyrene oligomers for each membrane. The addition of MOF to the unmodified P84 membrane (UF(D) to ISG(D)) increased the rejection of the membrane but not significantly enough to place the membrane MWCO into the nanofiltration range. The chemically modified MOF membrane ISG(D) showed an
increased in rejection above the plain P84 membrane, UF(D), and also the chemically modified membrane, UF(D)-CMA. The MWCO of the ISG(D)-CMA membrane is within the nanofiltration range at 795 g mol$^{-1}$. The MOF membrane grown on chemically modified UF membrane, ISG(D)-CMA, outperforms the MOF membrane grown on plain P84, ISG(D) in both rejection and permeance. The use of chemical modification agent avoids the defects associated with uncontrolled growth in the ISG(D) membrane, that do not allow for that membrane to have a MWCOs in the nanofiltration range.

**Figure 48:** MWCO curves for P84 membranes (UF(D)), surface modified P84 membrane (UF(D)-CMA), the MOF modified membranes (ISG(D) and ISG(D)-CMA) tested at 10 bar with polystyrene in acetone solvent. The mean data for each membrane is plotted, with the error bars representing one standard deviation.

The rejection of the chemically modified MOF membrane (ISG(D)-CMA) was compared to the rejection of a pure HKUST-1 film as predicted by the pore flow model as described by Bowen and Welfoot[177] (see Equation 13) and used by Stawikowska et al.[123] used to model the rejection of polymer ISA nanofiltration membranes.

The diameters of the polystyrene markers were estimated by drawing the chemical structure of each molecule in ChemBio3D Ultra 13.0 and minimising the energy of the molecules to find the most likely configuration. The dimensional lengths of the molecules were then used to calculate the rejections of the molecules. ChemBio3D Ultra 13.0 calculates the dimensions of molecules with minimised energy in a vacuum, and while it can be assumed that the configuration and/or size of the polystyrene molecules in acetone differs from that found in vacuum, the sizes calculated allow for a reasonable approximation of the separation properties of HKUST-1 films.
The given pore size of the HKUST-1 film was 0.9 nm[196, 197]. It can be seen in Figure 49 that the rejection for the ISG(D)-CMA membrane does not reach the rejections predicted by the pore flow model. This suggests that the HKUST-1 within the membrane is not completely defect free, and does not completely control the rejection of solutes in the membrane.

Figure 49: MWCO curves for chemically modified MOF membrane (ISG(D)-CMA) tested at 10 bar with polystyrene in acetone solvent compared to rejection of a pure HKUST-1 film predicted by the pore flow model.

While the ISG(D)-CMA membrane displayed the highest solute retentions of all the membranes, physical evidence of improved growth characteristics of MOF in ISG(D)-CMA membranes is less conclusive. Addition of MOF material to a membrane should result in an increase in the weight of the membrane. The mass, density and thickness of the membranes can be found in Table 13.

Table 13: Thickness, mass per square metre, density and surface area of the denser membranes used in this study.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
<th>Mass (g.m⁻²)</th>
<th>Density (g.cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF(D)</td>
<td>67 ± 1</td>
<td>43 ± 3</td>
<td>0.64 ± 0.05</td>
</tr>
<tr>
<td>ISG(D)</td>
<td>65 ± 3</td>
<td>63 ± 2</td>
<td>0.97 ± 0.06</td>
</tr>
<tr>
<td>UF(D)-CMA</td>
<td>73 ± 4</td>
<td>55 ± 0</td>
<td>0.6 ± 0.01</td>
</tr>
<tr>
<td>ISG(D)-CMA</td>
<td>78 ± 2</td>
<td>53 ± 5</td>
<td>0.68 ± 0.05</td>
</tr>
</tbody>
</table>
The densities of the ISG(D) and ISG(D)-CMA membranes are higher than the non-MOF membranes (UF(D) and UF(D)-CMA respectively) from which they are formed. However, the increase in density is lower from UF(D)-CMA to ISG(D)-CMA than for UF(D) to ISG(D), indicating that the amount of MOF grown in the ISG(D)-CMA membrane is lower than the ISG(D) membrane.

The presence of crystalline HKUST-1 material in hybrid polymer/MOF membranes was confirmed using X-ray powder diffraction (XRPD). Figure 50 shows the XRPD data for each of the membranes, compared to the XRPD of pure HKUST-1 crystals. The non-MOF membranes (UF(D) and UF(D)-CMA) show no sign of MOF crystallinity, and they have very similar XRPD readings to each other. The characteristic peaks of HKUST-1 occur at 2θ angles 6.6, 9.4, 11.5 and 13.3, the ISG(D) membrane shows large peaks at these values. The ISG(D)-CMA membrane only has one small peak at 13.3, confirming that the amount of HKUST-1 grown in the chemically modified membrane is less than the membrane without CMA addition.

Figure 50: XRPD data for the membranes alongside the data for pure HKUST-1 crystals
Figure 51: SEM image of membrane ISG(D) used to find point spectrum EDX data. The data can be found in Table 14

Table 14: EDX elemental analysis for the ISG(D) membrane, each spectrum point corresponds to the point indicated in Figure 51

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Element</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon</td>
<td>72.87</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>21.85</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>5.14</td>
</tr>
<tr>
<td>2</td>
<td>Carbon</td>
<td>73.44</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>21.58</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>4.98</td>
</tr>
<tr>
<td>3</td>
<td>Carbon</td>
<td>76.7</td>
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<tr>
<td></td>
<td>Oxygen</td>
<td>15.8</td>
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<tr>
<td></td>
<td>Copper</td>
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<td>4</td>
<td>Carbon</td>
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<td></td>
<td>Oxygen</td>
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<tr>
<td></td>
<td>Copper</td>
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<td>5</td>
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<td></td>
<td>Oxygen</td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>2.62</td>
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</tbody>
</table>

Table 14 shows the percentage of copper measured throughout the cross-section of the ISG(D) membranes at given points shown in Figure 51. The EDX data suggests that atomically between 3% and 8% of the ISG(D) membrane is copper, confirming the presence of HKUST-1 material in these membranes. Table 15 shows the percentage of copper measured throughout the cross-section of the ISG(D)-CMA membrane at given points shown in Figure 52. The EDX data for the ISG(D)-CMA membrane shows that the concentration of copper throughout the membrane ranges from 0% to just below 3%, once again indicating that this membrane actually contains less HKUST-1 material than the ISG(D) membrane.
Figure 52: SEM image of ISG(D)-CMA membrane used to find point spectrum EDX data. The data can be found in Table 15

Table 15: EDX elemental analysis for membrane ISG(D)-CMA, each spectrum point corresponds to the point indicated in Figure 52

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Element</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon</td>
<td>67.35</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>31.04</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>0.21</td>
</tr>
<tr>
<td>2</td>
<td>Carbon</td>
<td>67.45</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>32.55</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Carbon</td>
<td>62.04</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>35.24</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>2.64</td>
</tr>
<tr>
<td>4</td>
<td>Carbon</td>
<td>60.46</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>36.79</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>2.64</td>
</tr>
<tr>
<td>5</td>
<td>Carbon</td>
<td>63.65</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>33.97</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Despite the rejection performance of the ISG(D)-CMA membrane being an improvement on the ISG(D) membrane the evidence from the XRD data, mass and density measurements and SEM/EDX data suggests that the membrane actually contained less HKUST-1 material. Therefore the addition of CMA does not cause an increase in growth of MOF within the membranes. However the MOF material that does grow may have better adhesion to the polymer surface, and the HKUST at the surface of the ISG(D)-CMA membrane could contain fewer defects than ISG(D) membranes. The ATR-FTIR spectrum of the ISG(D)-CMA membrane shows that the membrane has a strong HKUST-1
signal at the membrane surface, suggesting that the ISG(D)-CMA membrane contains a very thin low defect MOF layer at the membrane surface. This could also explain the high permeance value measured for the membrane.

5.4 Conclusions

This chapter details a number of ways in which the performances of in-situ growth (ISG) membranes can be improved. The main methodologies for improving the performances of these membranes were to alter the parameter controlling MOF growth, altering the physical parameters of the membrane and altering the chemical nature of the membranes. While altering the parameters controlling the growth of HKUST-1 in ISG membranes did little to improve membrane performances, altering the nature of the polymer membrane scaffolds did improve solute retentions.

It was shown that the performance of hybrid polymer/MOF membranes, both MMMs and ISG membranes, can be improved by incorporating HKUST-1 into dense polymer support membranes. Increasing the density improves the rejection performance of polymer membranes. The hybrid polymer/MOF membranes produced with dense membranes also have improved rejections. While the changes in rejection and permeance for the MMMs are similar to the changes observed for the UF membranes, the changes for the ISG membranes are more favourable. The reduction in permeance of the ISG(D) is less than the other membranes while the increase in rejection is greater.

This chapter demonstrated that the performance of ISG(D) hybrid polymer/MOF membranes can be further improved through the use of a chemical modification agent (CMA) to encourage direct MOF growth on the pore walls of the polymer membrane. The ISG(D)-CMA membranes were characterised using a number of analytical methodologies, include ATR-FTIR, SEM/EDX, XRD and mass and density analysis. These membrane characterisation methodologies indicated that the mass of HKUST-1 grown in the ISG(D)-CMA membranes was lower than in the non-chemically treated ISG(D) membranes. Despite the lower mass of HKUST-1 growth, the high solute retentions and the ATR-FTIR data suggests that the HKUST-1 had good adhesion to the membrane surface, and possibly formed a low-defect, thin film on the surface of the membrane. The fabrication and utilisation of hybrid thin film MOF/polymer membranes is further discussed in Chapter 6.
Chapter 6

6. Development of Hybrid Thin Film MOF/Polymer Membranes

6.1 Introduction

In Chapters 4 and 5 in-situ growth (ISG) membranes were shown to outperform mixed matrix membranes (MMMs) for organic solvent nanofiltration (OSN) applications. ISG membranes have improved selectivity in both gas separations[54], and OSN applications (as shown in Chapter 4) above that of both polymeric integrally skinned asymmetric (ISA) membranes and MMMs. However ISG membranes have been shown to have low permeance performances. In order to improve solvent permeance through hybrid MOF/Polymer membranes a fabrication methodology to produce MOF thin film composite membranes (MOF-TFCs) has been developed.

Thin film composite (TFC) membranes consist of a separate thin selective layer on top of a porous support layer made from a different material[102]. TFC membranes have higher fluxes as compared to ISA membranes due to their ultrathin selective layers, and the highly porous support layers which offer little resistance to solvent flux. The permeance performances of hybrid inorganic/polymer membranes containing MOFs could also be improved by fabricating thin MOF films via interfacial synthesis.

Until recently fabrication of MOF films has focused either on direct growth via solvothermal synthesis onto a substrate surface, or layer by layer deposition[225-228]. These methodologies can lead to the formation of thick films (over 10 microns), with defects, and are difficult to scale-up. Forming MOF thin films via interfacial synthesis is likely to result in thinner films, with fewer defects. Ameloot et al. developed a methodology to fabricate hollow capsules of HKUST-1 using interfacial synthesis[174], the MOF films surrounding these capsules were under 1 micron thick and were defect free. During interfacial synthesis the reagents primarily meet and react at the sites of any remaining defects, meaning films are self-completing. Forming thin MOF films via interfacial synthesis could be achieved using the same technology used to produce commercial TFC membranes. MOF thin films formed via interfacial synthesis have been used for gas separation processes[55], but are yet to be tested for OSN applications.

This chapter reports the use of interfacial synthesis to produce thin films of MOF HKUST-1 on Polyimide P84 support membranes (MOF-TFCs). Producing MOF thin films via interfacial synthesis should produce membranes with improved permeance compared to ISG membranes, with similar retention properties. The permeance performances are tested in OSN conditions and recorded to test whether using MOF thin films reduces the resistance to solvent permeance. SEM/EDX was used to explore the structure of the hybrid membranes and the position of the HKUST-1 film.

6.1.1 Chapter Aims

This chapter aims to describe the development of hybrid thin film MOF/polymer membranes fabricated via interfacial synthesis. It should be demonstrated that, by using two immiscible liquids, the growth of a MOF film can be orientated at the surface of a polymer membrane. The MOF-TFCs produced will be used in OSN conditions to test the hypothesis that reducing the thickness of the selective MOF layer increases the permeances achievable for hybrid polymer/MOF membranes. The
MOF-TFCs will need to retain the selective nature of the ISG membrane, with improved permeance performances.

6.2 Experimental

6.2.1 Materials

The materials used in this chapter are identical to those used in Chapters 5 and 6 (see section 5.2.1 Materials). With the addition of copper acetate monohydrate and octanol purchased from Sigma Aldrich.

6.2.2 Membrane Preparation

Polymer ultrafiltration UF membranes were produced using the same methodology as described in Chapter 4 (see section 4.2.2 Membrane Preparation). While UF(D) membranes were produced according to the parameters described in Chapter 5 (see section 5.2.2 Membrane Preparation).

Hybrid polymer/MOF in-situ growth (ISG) membranes were fabricated using the processes described in Chapter 4 (see section 4.2.2 Membrane Preparation). While ISG (D) membranes were produced according to the parameters described in Chapter 5 (see section 5.2.2 Membrane Preparation).

MOF thin film composite membranes (MOF-TFCs) were produced via interfacial synthesis of HKUST-1 films on to P84 polymer ultrafiltration membranes, both UF and UF(D). The thin film fabrication methodology was based on the research carried out by Ameloot et al.[174]. Two fabrication methodologies were devised in order to ascertain the influence of solvent position on film fabrication.

**Figure 53:** Schematic representation of fabrication method A, wherein the P84 support membrane is impregnated with copper acetate in water and of fabrication method B wherein the P84 support membrane is impregnated with benzene tricarboxylic acid (BTC) in octanol. The membranes are initially taped to the bottom of a petri dish by tape (red), in Step 1 the membrane impregnated by copper acetate is green, while the membrane impregnated by benzene tricarboxylic acid remains yellow. In Step 2 the membranes are completely covered by BTC in octanol solution (method A: represented by grey) and copper acetate in aqueous solution (method B: represented by blue). In Step 3 the tape is removed and the uncovered membranes have changed colour to blue.
Fabrication Methodology A

A piece of polymer ultrafiltration membrane was soaked in a 70 g.L\(^{-1}\) solution of copper acetate in water. The membrane was removed from the solution, and excess solution removed from the surface of the membrane. The membrane was then taped to the bottom of a petri dish and a 17g.L\(^{-1}\) solution of 1,3,5-benzene tricarboxylic acid in octanol poured on top of the membrane.

Fabrication Methodology B

A piece of polymer ultrafiltration membrane was soaked in a 17 g.L\(^{-1}\) solution of 1,3,5-benzenetricarboxylic acid in octanol. The membrane was removed from the solution, and excess solution removed from the surface of the membrane. The membrane was then taped to the bottom of a petri dish and a 70g.L\(^{-1}\) solution of copper acetate in water poured on top of the membrane.

Before testing, membranes were conditioned with a PEG400:IPA (60:40 v/v) solution for 12 hours.

6.2.3 Copper Acetate Solubility and Diffusion Measurements

A saturated solution of copper acetate was produced by adding an excess mass of copper acetate (0.0118g) to 20 ml of octanol, the solution was left for 48 hours, to maximise dissolution. Visible copper acetate crystals could be seen at the bottom of the solution, ensuring that the solution was saturated. The concentration of the saturated solution was measured using a Shimadzu UV-1800 UV-Vis spectrophotometer. The diffusion of copper acetate from aqueous solutions to octanol was found by adding pure octanol to aqueous 70 g L\(^{-1}\) solutions of copper acetate. As the liquids are immiscible, and octanol has a lower density than water, the octanol floated on top of the aqueous solution. After periodic time intervals the concentration of copper acetate in the octanol solutions was measured using the same Shimadzu UV-1800 UV-Vis spectrophotometer.

6.2.4 Membrane Characterisation

Membrane mass, thickness and density measurements were carried out via the methodology described in Chapter 4 (see section 4.2.3 Membrane Characterisation).

Scanning electron microscopy (SEM) was carried out using a high resolution SEM microscope as described in Chapter 3 (see section 3.2.5 Scanning Electron Microscopy). EDX analysis was conducted according to the parameters described in Chapter 4 (see section 4.2.3 Membrane Characterisation).

ATR-FTIR data was collected using the same procedure as stated in Chapter 3 (see section 3.2.7 ATR-FTIR).

6.2.5 OSN Experimental Procedure

UF, ISG and MOF-TFC membranes were tested in cross-flow filtration set-up, using at least 2 separate discs from separate membrane sheets. UF(D), ISG(D) and MOF-TFC(D) membranes were tested in dead end filtration cells with a single disc of each membrane tested. All filtration experiments were carried out at 10 bar using the same polystyrene/acetone model solution described in Chapter 3. Membrane permeances and solute rejections were recorded using the same procedure as described in Chapter 3 (see section 3.2.8 OSN Experimental Procedure).
6.3 Results and Discussion

6.3.1 Fabrication Methodology A

The initial colour of the copper acetate impregnated polyimide P84 membrane was green. After four hours of exposure to the octanol/benzene tricarboxylic acid solution the membrane colour had changed to blue. The colour change suggests that a layer of HKUST-1 MOF had grown on the surface of the membrane. Figure 54 shows cracks appearing in this HKUST-1 film. The MOF delaminates from the membrane, revealing the polymer surface below. The cracks that occurred in the HKUST-1 layer did not form instantaneously. This indicates that the extent of the reaction and the growth of the HKUST-1 layer are dependent on time.

![Figure 54: Cracking HKUST-1 layer caused by overgrowth of MOF layer on top of a P84 support membrane](image)

Figure 55 shows the growth of a HKUST-1 layer grown at the interface of a solution of copper acetate in water (blue) and 1,3,5-benzenetricarboxylic acid in octanol (colourless). A light blue HKUST-1 layer is visible after just 1 minute, and the layer continues to get thicker for the next 2 hours. The growth of MOF does not appear to be restricted as the MOF film grows. The continual growth of HKUST-1 in the thin film membranes could be the cause of the cracks in the hybrid thin film membranes. Figure 56 shows the growth of the HKUST-1 layer from above. At 1 minute the HKUST-1 layer still appears to contain defects, while after 10 minutes the film appears fully formed and defect free.
Hybrid MOF thin film membranes were fabricated and the reaction times altered to test the effect of time on film formation. Figure 57 shows two membranes formed with reaction times of 1 minute and 15 minutes. The image of the membrane formed after 1 minute shows that a thin MOF film can be formed after just 1 minute of reaction time. If the membrane is left for 15 minutes the MOF
begins to break apart, suggesting that the process is time sensitive and over growth of the MOF film can cause the HKUST-1 to crack.

**Figure 57**: (left) MOF-TFC after 1 minute of reaction time, (right) MOF-TFC after 15 minutes of reaction time

Unfortunately, the HKUST-1 film formed after 1 minute of reaction time began to crack and flake once the membrane was removed from IPA solution, making these membranes unsuitable for application. The HKUST-1 MOF layer is brittle and does not chemically bond to the polymer support layer beneath. In order to produce membranes that can be used for OSN applications the HKUST-1 film must be firmly attached to the polymer support membrane.

**Figure 58**: Diagram demonstrating the diffusion of copper acetate molecules causing the MOF film to be formed on the octanol side of the solution.
Copper acetate was found to be slightly soluble in octanol, reaching saturation at $0.645 \pm 0.08 \text{ g L}^{-1}$, it is theorized that the HKUST-1 crystallisation reaction occurs above the aqueous/organic interface (See Figure 58). Copper acetate molecules could diffuse across the interface from the water solution inside the membrane into the octanol solution and react with the 1,3,5-benzenetricarboxylic acid. The diffusion of copper acetate from concentrated aqueous solutions into the octanol phase was measured over time (see Figure 59). After just a short time the concentration of copper acetate in the octanol portion of the solutions has reached values comparable to saturated solutions.

**Figure 59:** Concentration with time of copper acetate in octanol solution. The copper acetate concentration increases over time due to diffusion from a 70 g L$^{-1}$ aqueous solution of copper acetate. The black crosses represent the measured copper acetate concentrations at given times. The black dashed line shows the trend line of increasing copper acetate concentration. The red dashed line represents the saturation concentration of copper acetate in octanol, while the pink and burgundy dashed lines above and below show the upper and lower bounds of the saturation concentration (1 standard deviation).

Due to the diffusion of copper acetate into octanol over time it is possible that the HKUST-1 formation reaction occurs just above the membrane surface when methodology A is employed. If the reagent mixtures are alternated, and the 1,3,5-benzenetricarboxylic acid solution is impregnated in the membrane the copper acetate molecules will diffuse into the membrane and the film should grow within the polymer matrix.
6.3.2 Fabrication Methodology B

After 24 hours of exposure to copper acetate solution polyimide P84 membranes, impregnated with 1,3,5-benzenetricarboxylic acid in octanol, turned from yellow to blue. SEM images (see Figure 60) show a dark band of HKUST-1 at the surface of the membrane. SEM-EDX (see Figure 61) confirms that the concentration of copper peaks sharply at the membrane surface, with another apparent peak at the bottom of the membrane. This is in stark contrast to the SEM-EDX of the ISG membrane (also shown in Figure 60), for which there is a high concentration of copper throughout the middle of the membrane. The SEM-EDX results suggest that using immiscible solutions of water and octanol restricts the reaction of HKUST-1 to the surfaces of the membrane.

Figure 60: SEM cross-section images of (A) UF membrane (1000x magnification) (B) ISG membrane (1000x magnification) (C) MOF- TFC membrane (1000x magnification) and (D) MOF-TFC membrane (10000x magnification)

Figure 61: (Left) SEM-EDX image of MOF-TFC membrane fabricated via methodology A, (Right) SEM-EDX image of ISG membrane. The red lines represent the concentration of copper throughout the cross-section of the membranes.
Exploring the structure of MOF-TFC membranes further, the SEM image in Figure 62, suggests that the MOF film grows just beneath the surface of the membrane. As previously discussed it is theorized that copper acetate molecules migrate across the liquid/liquid interface from the water solution into the octanol solution. As the octanol solution is inside the membrane, the MOF film grows just inside the membrane surface when fabrication methodology B is employed. This means that the HKUST-1 layer is firmly embedded into the membrane structure. As the MOF film is physically embedded into the polymer layer the brittle nature of HKUST-1 is negated and therefore cracks and defects are less likely to occur post-film fabrication.

Figure 63: ATR-FTIR Spectra for UF, ISG and MOF-TFC membrane fabricated via methodology B, indicating that HKUST-1 has been successfully incorporated onto the surface of the MOF-TFC membrane.
Figure 63 shows the ATR-FTIR spectra of the membranes as compared to the spectrum of pure HKUST-1 powder. The characteristic peaks of HKUST-1 bonds are identified as occurring at 740, 1380 and 1450 cm\(^{-1}\). While the UF membrane displays no evidence of peaks at these wavenumbers, both the ISG and MOF-TFC membranes have peaks which occur at these points. Figure 63 confirms the presence of HKUST-1 in the MOF-TFC membranes.

Table 16 shows the thickness, mass and density of the pure polymer membrane (UF), uncontrolled \textit{in-situ} growth membrane (ISG) and the thin film MOF membrane (MOF-TFC). The change in mass and density of the MOF-TFC membrane is significantly less than the changes measured for the ISG membrane, indicating that there is less MOF in the MOF-TFC membrane. Less HKUST-1 material has grown in the MOF-TFC, as the crystal growth is restricted to a thin band at the surface of the membrane. The MOF-TFC membranes fabricated via methodology B were found to be flexible as the MOF film is embedded in the polymer film, and thus the membranes were tested in OSN conditions.

Table 16: Thickness, mass and density of Membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
<th>Mass (g m(^{-2}))</th>
<th>Density (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>100</td>
<td>57</td>
<td>0.57</td>
</tr>
<tr>
<td>ISG</td>
<td>107</td>
<td>88</td>
<td>0.82</td>
</tr>
<tr>
<td>MOF-TFC</td>
<td>101</td>
<td>62</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Figure 64: Rejection of polystyrene markers in acetone at 10 bar applied pressure. Mean data for each membrane plotted, error bars show one standard deviation.
Table 17: Permeance data for polymer (UF) and hybrid polymer/MOF membranes (ISG & MOF-TFC)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeance (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>131 ± 11</td>
</tr>
<tr>
<td>ISG</td>
<td>16.1 ± 0.9</td>
</tr>
<tr>
<td>MOF-TFC</td>
<td>54.0 ± 16.0</td>
</tr>
</tbody>
</table>

Figure 64 shows that the selective nature of the membrane has not been adversely affected as the solute retentions of the MOF-TFC and ISG membrane are similar. Table 17 shows that the MOF-TFC membrane has a permeance over three times higher than the ISG membrane. Producing a thin MOF thin, rather than the undirected growth of the ISG membrane, reduces the resistance to flow in the membranes, resulting in higher permeance performances.

Figure 65: Rejection of polystyrene markers in acetone at 10 bar applied pressure

Table 18: Permeance Data for dense polymer (UF(D)) and hybrid MOF membranes (ISG(D) & MOF-TFC (D))

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeance (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF (D)</td>
<td>33.9</td>
</tr>
<tr>
<td>ISG (D)</td>
<td>3.6</td>
</tr>
<tr>
<td>MOF-TFC (D)</td>
<td>14.0</td>
</tr>
</tbody>
</table>
As previously reported in Chapter 5, the rejection performances of ISG membranes are heavily dependent on the base polymer membrane performance. The same can be said for MOF-TFC membranes. Figure 65 shows that using a dense polymer support (UF(D)) also improves the performance of the MOF-TFC membrane. Table 18 shows that even with improved rejection performances the permeance of the MOF-TFC membrane is almost four times higher than the permeance of the ISG membrane.

The performance of the MOF-TFC membranes indicates that this hybrid membrane fabrication methodology is an improvement on ISG for OSN applications, and by extension MMMs. While retention results are just as high for MOF-TFCs as ISG membranes, the permeance performances are three to four times higher.

6.4 Conclusions

This chapter shows that there is potential for using hybrid thin film MOF/polymer membranes for organic solvent nanofiltration (OSN) applications. MOF-TFC membranes, containing thin films of the MOF HKUST-1, were produced via interfacial synthesis at the interface of immiscible solutions of water and octanol, designed to orient the MOF film at the surface of a polymeric ultrafiltration membrane. Two methodologies were employed to produce MOF-TFC membranes; methodology A, where an aqueous copper acetate solution is impregnated in a polymeric membrane, and methodology B, where a polymeric membrane is impregnated with a solution of 1,3,5-benzenetricarboxylic acid in octanol. Inversion of the solutions was shown to heavily influence the positioning of the MOF film, with methodology A leading to film growth outside of the membrane, causing the film to delaminate from the membrane surface. Membranes produced by methodology A were thus unsuitable for separation processes. SEM/EDX analysis showed that using methodology B leads to HKUST-1 grown within the membrane surface; subsequently these membranes were tested in OSN conditions.

The rejection and permeance performances of MOF-TFC membranes were tested using polystyrene markers in acetone solvent. The performances of these membranes were compared to polymeric ultrafiltration membranes and hybrid polymer/MOF in-situ growth (ISG) membranes. MOF-TFC membranes were found to have higher solute retentions than polymeric ultrafiltration membranes, demonstrating that the MOF thin film had augmented the selective layer of the polymeric membrane. MOF-TFCs were shown to have similar retentions to the existing ISG hybrid polymer/MOF membrane fabrication methodology, however solvent fluxes were 3 to 4 times higher since the thin MOF selective layer is less restrictive to solvent flow.
Chapter 7


7.1 Introduction

In Chapters 4 and 5 in-situ growth (ISG) was demonstrated as a viable methodology to produce hybrid polymer/MOF membranes using copper based MOF HKUST-1 and polyimide membranes. An alternative MOF was chosen to create ISG membranes as a comparison to the HKUST-1 ISG membranes. Iron based MOFs, Fe-BTC and MIL-101, were chosen, as they contain the same organic linker as HKUST-1, benzene tricarboxylic acid, which may aid adhesion between the MOF and polymer phase of ISG membranes. Iron based MOFs are also of interest for use in catalytic processes.

The fabrication of HKUST-1 based ISG membranes was possible because the MOF can be fabricated at room temperature; this was confirmed in Chapter 3 of this thesis. HKUST-1 also has a distinct, well characterised X-ray powder diffraction pattern (XRPD), this can be used to confirm the presence of MOF in ISG membranes. The fabrication methodologies and characteristics of MOFs all differ, and therefore the production of ISG membranes using different MOFs may not be as simple as HKUST-1. Iron based MOFs containing BTC come in two main forms MIL-101 and Fe-BTC. Differences in the reagents used to produce these membranes results in different porous structures.

Hybrid polymer/metal organic framework (MOF) membranes, both MMMs and ISGs were produced using iron based MOFs and polymer polyimide UF support membranes. The permeability and rejection performances of the membranes were compared to each other and traditional polymeric integrally skinned asymmetric (ISA) membranes. The swelling behaviour of these membranes in acetone was assessed, as well as their compaction under pressure, in order to understand the phenomena of flux decline in these hybrid membranes.

Flux decline was measured over a 24 hour period. The thickness change of membranes exposed to pressure and the swelling of the membranes in acetone were measured to assess whether physical changes in the membrane structure could influence flux decline. Also thickness measurements were used to determine whether the rigidity of MOF particles facilitated a reduction in flux decline.

7.1.1. Chapter Aims

This chapter aims to fabricate hybrid polymer/MOF in-situ growth (ISG) and mixed matrix membranes (MMM) using the iron based MOFs and test them in OSN conditions. The membrane fabrication methodology employed to create ISG membranes will be the same as that used to make ISG membranes using the copper based MOF HKUST-1, except iron salts will be used in place of copper nitrate. The structure of these membranes will be assessed using XRPD and SEM. The performances of these membranes were observed to assess the application of hybrid polymer/MOF membranes using iron based MOFs in OSN.
7.2 Experimental

7.2.1 Materials

The materials used in this chapter are identical to those used in Chapters 3 & 4 (see section 3.2.1 Materials). With the addition of iron nitrate trihydrate and iron chloride purchased from VWR International and Fe-BTC powder (Basolite F300) purchased from Sigma Aldrich.

7.2.2 Membrane Preparation

Polymer ultrafiltration (UF) membranes were produced as described in Chapter 4 (See section 4.2.2 Membrane Preparation).

MMM-Fe membranes were prepared by dispersing Fe-BTC particles in P84 dope solutions with 24 wt% of polymer in DMF. The ratio of polymer to MOF by weight in the dope solutions was 5:1. MMM-Fe membranes were then cast, crosslinked and conditioned according to the procedure used to produce MMMs containing HKUST-1 (See section 4.2.2 Membrane Preparation).

Hybrid polymer/MOF in-situ growth (ISG) membranes containing iron based MOFs were fabricated using polymer UF membranes as structural scaffolds. ISG-Fe membranes were prepared by immersing polymer UF membranes into a fresh mixture of iron nitrate or iron chloride (5 g L⁻¹ in Ethanol solution) and 1,3,5-benzenetricarboxylic acid (2.5 g L⁻¹ in DMF solution). The membranes were left stirring in solution for 24 hours, and then were extensively washed with DMF to remove any unreacted reagents. Before testing, the membranes were conditioned with a PEG400:IPA (60:40 v/v) solution for 12 hours.

7.2.3 Membrane Characterisation

High resolution scanning electron microscopy (SEM) images were obtained using the same methodology described in Chapter 3 (see section 3.2.5 Scanning Electron Microscopy).

X-ray powder diffraction (XRPD) was carried out according to the procedure described in Chapter 3 (see section 3.2.4 X-Ray Powder Diffraction).

7.2.4. OSN Experimental Procedure

Each membrane (UF, MMM-Fe and ISG-Fe) was tested using cross-flow filtration cells at 10 bar applied pressure. The membrane performances were found by measuring the permeance and rejection of polystyrene/acetone solutions, as described in Chapter 3 (see section 3.2.8 OSN Experimental Procedure).

7.3 Results and Discussion

The iron MOF fabrication methodology using iron chloride yielded no solid material in either the bulk solution or the membrane, suggesting that MIL-100(Fe) does not readily form at ambient temperatures. Typically MIL-100(Fe) is fabricated via hydrothermal synthesis at 150 °C for 6 days using iron powder in acidic conditions and benzene tricarboxylic acid[204]. These conditions would lead to the destruction of the polyimide support membrane. However fabrication of iron based
MOF has been conducted using iron chloride (FeCl$_2$) and benzene carboxylic acid in ethanol at 70 ºC[201]. When the reaction was carried out at room temperature no MOF crystals were formed.

The iron MOF fabrication methodology using iron nitrate, designed to mimic the fabrication of HKUST-1 did produce solid material, however, rather than form crystals the solution solidified into a gel-like mass. Once the UF membrane was removed from the gel the membrane surface appeared red in colour. Confirmation of the formation of iron MOF Fe-BTC inside the ISG-Fe membrane was undertaken using XRPD. The results of the XRPD analysis can be found in Figure 66.

![Figure 66: XRPD Data for Basolite F300 powder and In-situ growth Fe-MOF membranes](image)

Figure 66 shows that the XRPD pattern for the ISG-Fe membrane has some similarity to the pattern of Basolite F300, the name for the commercially obtained Fe-BTC MOF supplied by Sigma Aldrich. The XRPD pattern for this material is not as clearly defined as the XRPD pattern for HKUST-1. This is because the crystalline structure of Fe-BTC is less clearly defined than HKUST-1[203].

As the reagents formed a gel like solid, the solvent molecules used to produce the ISG membranes must have been trapped in the solid matrix of the Fe-BTC. The effects of organic solvent swelling and drying on the membranes were tested. The results can be found in Table 19.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness Change in Acetone (%)</th>
<th>Thickness Change When Dried (%)</th>
<th>Overall Thickness Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>6.2</td>
<td>-20.8</td>
<td>-15.9</td>
</tr>
<tr>
<td>MMM-Fe</td>
<td>6.1</td>
<td>-15.8</td>
<td>-10.7</td>
</tr>
<tr>
<td>ISG-Fe</td>
<td>-7.5</td>
<td>-25.4</td>
<td>-31.0</td>
</tr>
</tbody>
</table>

Table 19: Membrane Swelling in Acetone, and Contraction after Drying
The thicknesses of PEG-400 conditioned UF, MMM-Fe and ISG-Fe membranes were measured using a Mitutoyo electronic thickness gauge. The membranes were submerged in acetone, at atmospheric pressure, to wash out the PEG-400 and any other solvents used in the fabrication of the membranes. After being submerged in acetone for 24 hours the thicknesses of the membranes were once again measured. The membranes were then removed from the solvent and allowed to dry completely. After allowing the membranes to dry for 24 hours the thicknesses were measured once again.

Table 19 shows that while the thicknesses of the polymer UF membrane and the MMM-Fe membrane increase after exposure to acetone, the ISG-Fe membrane shrinks in the presence of acetone. This suggests that the polyimide P84 membranes swell in the presence of acetone. However washing out the larger solvent molecules of IPA, DMF, Ethanol and PEG-400 from the Fe-BTC layer of the ISG membranes, and replacing them with acetone causes the membrane to contract. When the membranes are dried, and solvent is removed from the membranes, the thicknesses of all the membranes are reduced. However the thickness of the ISG-Fe membrane reduces more than both the polymer UF membrane and the MMM-Fe membrane. This suggests that ISG-Fe membranes are susceptible to the effects of solvent swelling.

Figure 67: SEM image of the surface of ISG-Fe Membrane

The surface of the ISG-Fe membrane can be seen in Figure 67 and Figure 68. There are many visible cracks on the surface of the membrane, which likely formed during the membrane drying process required to conduct SEM. The cracks on the surface of the membrane suggest a layer of ISG-Fe of significant thickness. SEM images and the thickness change measurements suggest that when the ISG-Fe membranes are formed from a thick gel layer of Fe-BTC and solvent is deposited on top of the membrane. Solvent makes up a significant amount of the MOFs formed, as shown by the measured changes in thickness. This trapped solvent may affect the performance of the ISG-Fe membranes over time as the trapped solvent in the Fe-BTC is removed from the membrane.
**Figure 68**: SEM image of the surface of ISG-Fe Membrane, (right) close up of a crack in the ISG-Fe layer

**Figure 69**: SEM image of the cross-section of ISG-Fe Membrane, (right) a close-up on a large ISG-Fe crystal in the polymer macrovoid

**Figure 70**: Cross-section of MMM-Fe membrane

**Figure 69** shows the cross-section of an ISG-Fe membrane. A large Fe-BTC crystal can be seen inside a macrovoid of the UF membrane. The shape of the crystal closely resembles the shape of
macrovoid, suggesting that the crystal has condensed from the reaction solution that filled the pores of membrane.

**Figure 70** shows the cross-section of the MMM-Fe membrane, where it can be seen that the Fe-BTC particle is firmly embedded into the polymer matrix and there is excellent adhesion between the MOF and the polymer. There are no visible non-selective voids in the membrane.

![Figure 70: Cross-section of the MMM-Fe membrane](image)

**Figure 71**: Permeability of 1 g L\(^{-1}\) PS in acetone solution at 10 bar

![Permeability Graph](image)

**Figure 72**: Rejection data of 1 g L\(^{-1}\) PS in acetone solution at 10 bar after (left) 1 hour and (right) 25 hours

![Rejection Graph](image)
The permeances of the membranes were measured over time, and the trends are shown in Figure 71. Unlike with HKUST-1 particles addition of Fe-BTC to polymer membranes in the form of a mixed matrix membrane increases permeance, though not by a large amount. As with the ISG of HKUST-1, the ISG-Fe membranes have the lowest permeances. The average permeance of the ISG-Fe membranes is around half that of polymer UF membranes, while for membranes fabricated using HKUST-1 there is a 10-fold reduction in permeance between UF and ISG membranes.

While permeances of ISG-Fe membranes are higher than the permeances of ISG membranes containing HKUST-1, the solute retentions are not as good. Figure 72 shows the molecular weight cut-off (MWCO) curves for the membranes after 1 and 25 hours. While the rejection of solutes stays largely the same for the MMM-Fe membrane, there are significant changes in the MWCO curves for both the UF membrane and the ISG-Fe membrane. After 1 hour all three membranes have similar average rejections, however, after 25 hours the rejection of the UF and ISG-Fe membranes shifts higher. At lower molecular weights of polystyrene, the rejections of the UF and ISG-Fe membrane are similar, for higher molecular weight solutes the rejection for ISG-Fe membranes are higher than the UF membranes. It can be seen in Figure 72 that the rejection data for the ISG-Fe membranes has a large amount of error, the large range in error shows that the membranes can differ wildly in rejection. The large error bars present on the MWCO curve of the ISG-Fe membrane could be due to defects on membrane surface. The thick gel layer of Fe-BTC on the membrane surface was shown to have cracks after drying; those cracks may exist before drying of the membrane, and could cause the solute retentions to vary.

Table 20: Compaction of Membrane after 24 hours of 10 bar pressure, in acetone solvent

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness Change in Acetone (%)</th>
<th>Thickness Change When Dried (%)</th>
<th>Overall Thickness Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>-6.8</td>
<td>-5.0</td>
<td>-11.3</td>
</tr>
<tr>
<td>MMM-Fe</td>
<td>-12.4</td>
<td>-6.3</td>
<td>-19.0</td>
</tr>
<tr>
<td>ISG-Fe</td>
<td>-20.6</td>
<td>-14.3</td>
<td>-32.1</td>
</tr>
</tbody>
</table>

The influences of pressure and solvent on the membranes were tested by measuring the change in thickness of the membranes after the filtration tests, the results of which can be found in Table 20. The ISG-Fe membranes had the lowest changes in thickness after both pressure induced compaction in acetone and after membrane drying. The large change in membrane thickness for the ISG-Fe membrane confirms that the Fe-BTC phase does not reduce compaction. Unlike HKUST-1 based hybrid membranes the Fe-BTC does not increase the physical strength of the membranes.

7.4 Conclusions

This chapter shows that hybrid polymer/MOF membranes can be produced with iron based MOFs, using both mixed matrix membrane and in-situ growth fabrication methodologies. Fabrication of ISG membranes using iron chloride to produce MIL-100(Fe) did not work, as fabrication of MIL-100(Fe) cannot occur at room temperature. ISG membranes were made using iron nitrate and benzene tricarboxylic acid to produce Fe-BTC. The growth of Fe-BTC within polymer membranes was confirmed using X-ray powder diffraction (XRPD).
SEM images of the ISG-Fe membranes showed that a thick layer of MOF grew on the surface of the polyimide P84 membranes, and also within the macrovoids of the membrane. SEM images of MMM containing commercially obtained Fe-BTC showed good adhesion between the polymer and MOF.

The hybrid membranes were tested in OSN conditions, and unlike hybrid membranes containing HKUST-1 there was no improvement in the solute retentions over polymer UF membranes. The permeance of the MMM-Fe membrane is higher than the polymer UF membrane; however rejections after 25 hours were worse than for the UF membrane.

The polystyrene rejections of the membranes were recorded after 1 hour and 25 hours of filtration of acetone solution. While rejections for the MMM-Fe membranes remained the same at both 1 and 25 hours, the rejections of the UF and ISG-Fe membranes increased. The highest rejections achieved were for the ISG-Fe membranes after 25 hours, however these membranes only achieved slightly better rejections than the UF membranes.

In conclusion this chapter shows that while fabrication of in-situ growth hybrid polymer/MOF membranes is possible, the membranes display no significant advantages over polymer membranes in either rejection or flux decline. This is in contrast to the results obtained for hybrid membrane fabrication using HKUST-1 as the MOF.
Chapter 8

8. Thesis Conclusions

The focus of this thesis was the design, fabrication and testing of hybrid polymer/metal organic framework (MOF) membranes. These membranes have been readily applied to gas separation processes, but their use in OSN applications has not yet been widely reported. The initial reason for investigating these membranes was to find flexible membranes with high flux, high rejections and highly organized surfaces, with regular porous structures. The hypothesis that the selectively nature of polymer membranes can be alter by the incorporation of MOFs to form hybrid membranes was shown to be true, though the influence of the MOFs was heavily influenced by the structure of the membranes formed.

A number of methodologies were developed to produce hybrid polymer/MOF membranes for OSN applications. While MMMs were initially investigated, the performances achieved using these membranes were found to be no significant improvement over polymer nanofiltration membranes. However, when ISG was utilised to alter the porous structure of polymeric ultrafiltration membranes the results were a lot more encouraging. Continual development of ISG membranes lead to fabrication the hybrid polymer/MOF membranes with high permeances, however defect-free MOF films were not achieved. A list of the main membranes tested in this thesis can be found in Table 21.

Table 21: List of prominent membranes tested in this thesis, with properties of the membranes included. The values in parenthesis refer

<table>
<thead>
<tr>
<th>Membrane Name</th>
<th>Membrane Type</th>
<th>MWCO (g mol⁻¹)</th>
<th>Rejection @ 995 g mol⁻¹ (%)</th>
<th>Permeance (L m⁻² h⁻¹ bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XL0</td>
<td>Nanofiltration - Polymer</td>
<td>1535</td>
<td>84</td>
<td>34</td>
</tr>
<tr>
<td>XL20</td>
<td>Nanofiltration - MMM</td>
<td>995</td>
<td>90</td>
<td>18</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration - Polymer</td>
<td>UF</td>
<td>18(8)</td>
<td>217(131)</td>
</tr>
<tr>
<td>UF(D)</td>
<td>Ultrafiltration - Polymer</td>
<td>UF</td>
<td>42</td>
<td>120</td>
</tr>
<tr>
<td>MMM</td>
<td>Ultrafiltration - MMM</td>
<td>UF</td>
<td>38</td>
<td>93</td>
</tr>
<tr>
<td>ISG</td>
<td>Hybrid ISG</td>
<td>UF</td>
<td>52(26)</td>
<td>18(16)</td>
</tr>
<tr>
<td>ISG(D)</td>
<td>Hybrid ISG</td>
<td>UF</td>
<td>79</td>
<td>15</td>
</tr>
<tr>
<td>ISG(D)-CMA</td>
<td>Hybrid ISG</td>
<td>795</td>
<td>92</td>
<td>66</td>
</tr>
<tr>
<td>MOF-TFC</td>
<td>Thin MOF film</td>
<td>UF</td>
<td>(23)</td>
<td>(54)</td>
</tr>
<tr>
<td>Ideal MOF-TFC</td>
<td>Thin MOF film - Theoretical</td>
<td>250</td>
<td>100</td>
<td>&gt;200</td>
</tr>
</tbody>
</table>

The hybrid membranes shown in Table 21 fall into 3 categories: MMM, ISG and MOF-TFC membranes. The addition of MOF was shown to have little influence on the retention properties of polymer nanofiltration membranes and in fact the addition of 20% MOF particles lowered the permeance by a factor of 2. When MMM fabrication was applied to ultrafiltration membranes similar effects were observed, though the increase in rejection was greater. Ultimately membrane characterisation evidence showed that MMMs with MOFs dispersed in ISA membranes have very little MOF material at the membrane surface. MMM fabrication incorporating MOF particles into the selective layer of TFC membranes can overcome this issue, as demonstrated by Sorribas et al.[158] and Basu et al.[70].
The best performing membrane was the ISG(D)-CMA, which had the highest rejections observed, as well as the second highest permeance of all the hybrid polymer MOF membranes. Membrane characterisation methods showed that this membrane likely consisted of a thin layer of MOF, making the membrane like a MOF-TFC in structure. The rejection performances of MOF-TFCs were disappointing, and while they can be improved by using dense membranes supports (as also demonstrated with ISG membranes) however the permeance is reduced to the level of ISG membranes.

This thesis shows that the structure of membranes can highly influence the expected performance of hybrid polymer/MOF membranes. Methodologies such as SEM-EDX and ATR-FTIR are essential in determining whether the MOF layer is continuous or discrete, and whether the MOF is located at the membrane surface.

Calculations of the theoretical rejection of an ideal defect free HKUST-1 film show that there is still much improvement needed to reach the rejection performances by the Bowen and Welfoot pore flow transport model. Calculations of the permeance of a thin film of MOF (between 1 and 4 µm) were made using Equation 11. For such thin films permeances well above 200 L m⁻² h⁻¹ bar⁻¹ are possible, and ultimately the overall permeance would be determined by the permeability of the support membrane.

8.1 Future Directions

ISG(D)-CMA membranes had the highest reported solute rejections of all the hybrid polymer/MOF membranes, along with high permeance values. However the rejection performances could be further improved, as it was shown that the rejections achieved were lower than the values predicted by the pore flow model. Characterisation of the ISG(D)-CMA membranes show that the mass of HKUST-1 in these membranes is low. Further exploration of the surface of these membranes using AFM and ATR-FTIR could lead to a better understanding of the structure of these membranes. Ultimately the aim of producing hybrid polymer/MOF ISG membranes is to produce defect free membranes.

There is also scope to improve the performances of MOF-TFC membranes, the rejections achieved with these membranes were not as high as the ISG(D)-CMA membranes, but theoretically interfacial synthesis should lead to the fabrication of self-completing MOF films. The position of the MOF films, either outside or inside the membrane surface, could be controlled by switching the orientation of the reactant solutions in and out of the membrane. The tested membranes were those with the MOF film embedded within the membrane surface. However MOF films orientated outside the membrane surface could be promising if the films could be made to chemically or physically bond to the polymer membrane surface.

Improving the adhesion between MOF thin films and polymer membranes could be achieved by altering of concentrations of the reagents. Reducing the concentration of the reagents used could lead to slower film growth, if the film was to grow more slowly defects in the film could be reduced, and also allow the film to adhere to the polymer surface. This could also be achieved through the use of chemical modifying agents, such as the 1,2,4-benzenetricarboxylic anhydride used in Chapter 5.
Ultimately once defect free hybrid polymer/MOF membranes can be produced, a number of different MOFs should be used to test the effect of different porous structures on membrane performance. Using MOFs with a range of different pores sizes should lead to different rejection performances being achieved. Iron based MOF, Fe-BTC, was used to create ISG-Fe membranes, however these membranes were not defect free. Other alternative MOFs used for separation processes include ZIF-7[168] ZIF-8[44, 47, 229, 230] and MIL-101[158], though it may be a challenge to find polymers compatible with the fabrication conditions of these materials. Creating defect free ISG membranes with a number of different MOFs could lead to the creation of membranes with tuneable MWCOs.
References

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