Pervaporation Membranes Based on Polymer of Intrinsic Microporosity

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Abstract

This project aimed to explore the application of representative of polymers of intrinsic microporosity (PIMs), PIM-1 in pervaporation (PV) for alcohol recovery. In the first part, PIM-1 was synthesized using the high temperature method. A free-standing PIM-1 membrane was fabricated and assessed for the alcohol recovery, it is conclude that the performance of a PIM-1 membrane (both flux and selectivity) in separation of butanol/water is superior to that of ethanol/water. For the improvement of membrane total flux to meet the demands of industrial application, PIM-1 based thin film composite (TFC) membranes were fabricated. Polyvinylidene fluoride (PVDF) support materials were prepared, the impressive flux of 9.08 kg m\(^{-2}\) h\(^{-1}\) is obtained via PVDF coated in PIM-1 solution, while maintaining the separation factor of 13.3, which is superior to the performance of a commercial PDMS membrane.

In the second part, various PIM-1 based mixed matrix membranes (MMMs) were prepared for the improvement of membrane performance. Different types of filler (graphene, Fe\(_3\)O\(_4\) and organosilicon network) were incorporated into the PIM-1 matrix. The PIM-1/graphene mixture was obtained by liquid phase exfoliation of graphite with PIM-1 polymer as stabilizer, PIM-1/graphene MMMs were prepared and assessed in the pervaporation of butanol/water. A small amount of graphene loading (around 0.018 wt%) in MMMs enable the enhancement of flux (2.03 kg m\(^{-2}\) h\(^{-1}\)); Fe\(_3\)O\(_4\) nanoparticles were prepared by a chemical coprecipitation technique and modified by oleic acid (OA), magnetic treatment of PIM-1/Fe\(_3\)O\(_4\) dispersions confirms Fe\(_3\)O\(_4\) nanoparticles generate heat under external AC driven magnetic field. The experimental flux result is slightly lower than the theoretical result predicted via Maxwell model; Organosilicon network was prepared using phenyltrimethoxysilane (PhTMS) as a precursor to generate an organosilicon network via hydrolysis and condensation. The morphologies of PIM-1 based MMMs were assessed by SEM and the membrane PV performance (flux and selectivity) was also tested. The incorporation of PhTMS and PPhS do not improve the flux and separation factor of the membrane as expected.
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Dedication


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Chapter 1  Introduction
1.1 Aim and Objectives

The overall aim of this project is to explore the application of polymers of intrinsic microporosity (PIMs) in pervaporation (PV) for alcohol recovery. PIM-1 based thin film composite (TFC) membranes and mixed matrix membranes (MMMs) were fabricated and assessed in the pervaporation of butanol/water mixtures.

The objectives of this project were as follows:

(1) To prepare and characterize PIM-1 polymer (Chapter 2)

(2) To fabricate free-standing PIM-1 membranes and assess the pervaporation performance for alcohol recovery (Chapter 3)

(3) To fabricate PIM-1 based TFC membranes, using PVDF supports made in the laboratory, to explore the effect of the support on TFC membrane performance (Chapter 4)

(4) To prepare and characterize PIM-1/Graphene MMMs for the improvement of membrane performance and maintenance of stability (Chapter 5)

(5) To prepare and characterize PIM-1/Fe$_3$O$_4$ MMMs, and to investigate the use of localized annealing by induction heating of the membrane in an alternating magnetic field (Chapter 6)

(6) To prepare PIM-1/Organosilicon network MMMs, using phenyltrimethoxysilane as a precursor to generate organosilicon network via hydrolysis and condensation, for the improvement of membrane performance (Chapter 7)

1.2 Membrane separation processes

In modern times, along with the lack of energy resources globally, green and sustainable development arouses people’s interest all over the world. Based on this phenomenon, energy conservation, waste minimization and zero discharge draws much attention, especially in the industrial field. From this point of view, membrane-based separation technology, as a low-energy consumption and clean energy technology, exhibits more potential compared with traditional energy-intensive
separation processes such as distillation. Over the past decade, the membrane separation industry has been thought of as a promising alternative in chemical processing. It is considered as a new frontier of chemical engineering and is also extensively applied in many fields, such as waste water treatment, seawater desalination, the food industry, medical applications and gas separation, as well as chemical raw materials extraction.\(^1\)

Membrane separation is defined as the process in which a feed mixture composed of two or more components is partially separated through a membrane, which plays a role as a selective barrier, under a driving force (normally pressure or concentration gradient). Certain types of component permeate freely while the permeation of other components is prevented.\(^2\) The process of membrane separation is demonstrated in Figure 1-1.

![Figure 1-1 Schematic diagram of membrane separation process\(^3\)](image)

According to the different industrial applications, several membrane processes are applied, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), dialysis (D), gas separation (GS) and pervaporation (PV). The driving forces can be gradients in pressure, temperature, concentration or electrical potential, which lead to the flow of the permeate through the membrane.\(^4\)

1.3 Classification of Membranes

Membranes can be classified in three main ways, which are membrane
materials, membrane structure and membrane porosity. In terms of the materials, the membrane could be polymeric, inorganic or hybrid materials.

In terms of structure, membranes can be classified into two types:

1. Symmetric membrane, which possesses a homogeneous structure in the whole membrane matrix. For example, isotropic microporous membrane and nonporous dense membrane. (Figure 1-2 a and b)

2. Asymmetric membrane, which possesses a heterogeneous structure from the surface through the membrane matrix. For example, Loeb-Sourirajan membrane and thin film composite membrane. (Figure 1-2 c and d)

![Figure 1-2 Schematic diagrams of the principal types of membranes](image)

In terms of membrane porosity, they can also be subdivided into two types:

1. Microporous membranes, which have a highly voided structure with randomly distributed pores, the pore size is in the range 0.01-10 μm. The interconnected pore structure leads to a wide distribution of pore size, therefore, the separation of solutes by microporous membranes mainly depends on the molecular size and pore size distribution. Normally, microporous membranes can be used in particle filtration, microfiltration and ultrafiltration.

2. Dense membranes, which are nonporous or have an effective pore size in the range 0.5-2 nm. The transfer of molecules involves the diffusion through the membrane via the driving force, such as concentration, pressure, or electrical potential gradient. The separation of different components in a mixture is achieved by the diffusivity and solubility in the membrane materials. Dense membranes are normally used in reverse osmosis, gas separation and pervaporation.¹
The transport mechanisms through a membrane relate to the pore size of the membrane. For porous membranes, if the pore size is in range of 0.1~10 \( \mu \text{m} \), the molecular transport in the membrane is by normal convective flow. When the pore size of the membrane is smaller than 100 nm, it will become smaller than the mean free path (\( \lambda \)) of gas molecules, which is normally in range of 50-200 nm, once the ratio of pore size to gas mean free path is less than 1, Knudsen diffusion dominates the molecular transport, in which the collision frequency between penetrant molecules and pore walls is higher than that with other molecules; at every collision with the pore walls, the molecules are reflected in random directions and move independently of all others. When the pore size of membranes decreases to the range of 0.5~20 nm, molecular sieving diffusion applies for the molecule separation; in this case, due to the extremely narrow pore radius, the molecule adsorption on the pore wall become noticeable.\(^1\) For the dense membranes, the solution–diffusion mechanism provides a description of the molecular transport and will be particularly discussed in a later section. It is noteworthy that molecular sieving diffusion is normally demonstrated in well-structured microporous materials, such as zeolites and ceramic membranes, while the solution-diffusion mechanisms is mainly considered in polymer-based membranes due to the partial overlap of pore diameter.

### 1.4 Porous Organic Polymer Materials

Porous Materials draw attention in the chemical industry for their high potential in the applications of separation, adsorption, gas storage and catalysis. Various types of pore exist in the structures of porous materials, such as voids, cavities and channels, which lead to high surface areas (normally 300-1500 \( \text{m}^2/\text{g} \)).\(^5\) Generally the porosity, which is the ratio of void volume in a material to the entire volume of the material, reflects the amount of pore space within the material, normally between 0.2-0.95.

According to the classification standard of porous materials which was issued by the International Union of Pure and Applied Chemistry (IUPAC),\(^6\) porous materials
can be subdivided by the difference of pore size:

(1) Materials which have pore sizes smaller than 2 nm are defined as microporous materials; they are able to separate or store small size molecules, and are mainly applied in gas separation and pervaporation.

(2) Materials which have pore sizes in the range from 2 nm to 50 nm are defined as mesoporous materials, which are mainly used in nanofiltration and ultrafiltration.

(3) Materials which have pore size larger than 50 nm are defined as macroporous materials, which are mainly used in microfiltration and particle filtration.

Currently, of various types of porous materials, porous organic polymer materials are extensively studied due to the excellent processability. Porous organic polymers are composed of the light elements, such as C, H, N, O, which endow low density to materials. With the incorporation of functional groups on a polymer (acid/base, aromatic, hydrophilic/ hydrophobic), the materials are able to be applied in a wide range of industrial fields. Due to the existence of aromatic structure on the backbone, the porous organic polymer material is thermally and chemically stable. Additionally, compared with inorganic porous materials, the porous organic polymer material is easier to process and scale-up, which provides the high potential to commercialization.

In terms of the structure, porous organic polymers can be divided into two types: crystalline and amorphous. The typical crystalline porous organic polymers include Covalent Organic Frameworks (COFs) and Triazine Based Frameworks (TBFs), and the representatives of amorphous porous organic polymer are Hypercrosslinked Polymer (HCPs), Conjugated Microporous Polymers (CMPs) and Polymers of Intrinsic Microporosity (PIMs).\textsuperscript{7,8}
1.4.1 Covalent Organic Frameworks (COFs)

Covalent Organic Frameworks (COFs) are typical crystalline porous organic polymers. They are composed of organic monomers, which contain the elements in the periodic table C, H, O and B. The organic monomers connect with each other to generate scaffolding of strong covalent bonds and form a symmetrical and repeatable structure. COFs possess excellent thermal stability, which can afford the temperature up to 500-600°C due to the exist of strong interactions from B-O bonds.

The first COF material, which is named COF-1, was synthesized by Yaghi and co-researchers in 2005. The 2D monomer was applied to synthesize a planar boroxine ring structure (Figure 1-3). The BET surface area of COF-1 is 711 m² g⁻¹. Since 2007, the 3D tetrahedral monomer was applied to synthesize new types of COFs, such as COF-102 and COF-103. Due to the 3D structure of the polymer, they possess higher BET surface areas, which are 3472 and 4210 m² g⁻¹ respectively.

![Figure 1-3 The chemical structure of COF-1](image)

1.4.2 Triazine-Based Frameworks (TBFs)

Triazine-Based Frameworks (TBFs) are another typical ordered crystalline porous organic polymer, which are also named covalent triazine frameworks (CFTs). They are synthesized by the ionothermal polymerization of aromatic nitrile monomer in presence of Lewis acid and generate crystalline polytriazines.

The first CFTs material is named CFT-1, which is prepared using
1,4-dicyanobenzene (DCB) monomer reacted in molten ZnCl₂ at 400 °C. The structure is shown in Figure 1-4, the BET surface area of CFT-1 is 791 m² g⁻¹, and the total pore volume of 0.4 cm³ g⁻¹ is obtained.

Figure 1-4 The chemical structure of CFT-1¹²

1.4.3 Hypercrosslinked Polymer (HCP)

Hypercrosslinked Polymer is a type of amorphous porous polymer which was first synthesized by Davankov and co-researchers in the early 1970s.¹³ By means of the hypercrosslinked structure of the polymer, high rigidity and low degree of segment packing is achieved, which enables the formation of a stable microporous structure. The most well-known HCPs originate from polystyrene and are produced by extensive crosslinking via Friedel-Crafts alkylation.¹⁴ Free radical polymerization was first carried out applying vinylbenzyl chloride (VBC) as monomer, with divinylbenzene (DVB) as crosslinking agent to form crosslinked copolymer. Then the Friedel-crafts alkylation reaction was carried out to obtain the hypercrosslinked polymer network (Figure 1-5). The BET surface areas for hypercrosslinked materials can be up to 2,090 m² g⁻¹.¹⁵
1.4.4 Conjugated Microporous Polymers (CMPs)

Conjugated Microporous Polymers (CMPs) consist of rigid conjugated skeletons. The first CMP was synthesized by the Cooper group in 2007, which is prepared by Sonogashira-Hagihara palladium coupling to combine aromatic halides with aromatic alkynes to form the conjugated network. Till now, a series of CMPs have been prepared for different applications, in which CMP-0 (Figure 1-6) is the original structure of conjugated network, its BET surface area is 1018 m² g⁻¹. CMPs possess high porosity and excellent chemical and thermal stability, due to the existence of a π-bond system in the network. It displays high potential in catalysis, gas storage, gas separation and clean energy.
1.4.5 Polymers of Intrinsic Microporosity (PIMs)

Polymers of Intrinsic Microporosity (PIMs) are a family of materials which have interconnected pore structure with high free volume. They were first reported in the University of Manchester by McKeown and colleagues.\textsuperscript{17} The idea of PIMs originates from research into phthalocyanine-based materials for catalytic applications. In previous phthalocyanine network polymers, the phthalocyanine units tended to aggregate into stacks due to non-covalent interactions, which reduced catalytic activity severely. Therefore, a strongly rigid and nonlinear linking group between phthalocyanine units was needed to form a space-inefficient packing structure, as well as to inhibit the polymer relaxation and the loss of microporosity. In 2001, a network polymer was successfully synthesized from 5,5’,6,6’- tetrahydroxy- 3,3’,3’- tetramethyl- 1,1’- spirobisindane (TTSBI) with 4,5- dichlorophthalonitrile. The spiro-centre in TTSBI guarantees the nonlinear structure and the fused rings provide the polymer rigidity. Phthalocyanine network polymers were formed with spiro-cyclic crosslinks which inhibit the aggregation of phthalocyanine components, and give rise to an amorphous microporous structure. (Figure 1-7) The polymer microporosity was determined by nitrogen adsorption measurements. High surface areas (in range of 500 – 1000 m\(^2\) g\(^{-1}\)) were obtained for phthalocyanine-based materials.

![Figure 1-7 The preparation of phthalocyanine-based microporous network polymer](image)

Reagents and conditions: (i) K\(_2\)CO\(_3\), DMF, 80 °C; (ii) metal salt, quinoline, 200 °C\textsuperscript{18}
In parallel, a non-network polymer was also explored. It was generally thought that non-network polymers always pack efficiently, since the macromolecular backbone normally bends and twists to maximize the intermolecular interactions. However, some special types of polymer could also possess a large amount of free volume, which exists in the form of void space. These voids present an interconnected structure which is similar to traditional microporous materials, although it arises for a linear polymer rather than a network structure. Therefore, such types of materials are also soluble and solution-based processing and characterization can be realized, which is superior to a network polymer.

Following this idea, PIM-1 was the first polymer which has a linear structure and microporous voids in the PIMs family. It is synthesized from the polymerization of TTSBI and tetrafluoroterephthalonitrile (TFTPN), the reaction is shown in Figure 1-8.

![Figure 1-8 Synthesis scheme of PIM-1 polymerization using TTSBI and TFTPN monomer](image)

Due to the existence of spiro-centre and the fused ring structure, PIM-1 has a rigid and contorted shape (Figure 1-9) which endows it with microporous properties. Additionally, its solution-based processing and promising BET surface area (up to 800 m² g⁻¹) aroused great interest. Peter Budd in the University of Manchester immediately found the potential of PIM-1, its unique advantage is that it is a linear polymer which is solution processable and microporous in dry state. It is considered as an ideal microporous polymer which can be applied in different kinds of processing for preparing membranes for scale-up, such as solvent casting and dip-coating. This gives rise to a range of potential applications, particularly in areas such as gas separation and pervaporation, where thin films and high permeability are desirable. The first commercial application of PIM-1 is in a sensor developed by 3M for use as
an end-of-life indicator for organic vapour absorbing cartridges.\textsuperscript{57,58} This application is based on the strong affinity of PIM-1 for organic vapours.

![Molecular model of PIM-1](image.png)

\textit{Figure 1-9 The molecular model of PIM-1}\textsuperscript{18}

The focus of the present work is the recovery of alcohols by pervaporation. For this purpose a membrane material needs to be (i) organophilic, so that dilute aqueous alcohol solutions can be concentrated up, (ii) highly permeable, to minimize the required membrane area, and (iii) able to be prepared in sufficient quantities for large-scale membrane manufacture. PIM-1 is an organophilic, high free volume, membrane-forming polymer readily prepared from commercially available starting materials, and was therefore selected as an ideal candidate for this application.

1.5 Pervaporation

1.5.1 The Pervaporation Process

The pervaporation process is a promising alternative to conventional energy-intensive technologies, such as extractive distillation, for the separation of liquid mixtures, as it is economical, safe and ecofriendly. It is also considered as a clean technology, especially well-suited for the treatment of volatile organic compounds.

Pervaporation is a membrane separation process in which the liquid mixture, containing two or more chemical components, transfers through a non-porous polymeric membrane, or a molecularly porous inorganic membrane, while using
vacuum or sweep gas as a driving force (Figure 1-10). The chemical components in the feed liquid absorb on one side of membrane, permeate through the membrane, and then evaporate on the other side of membrane in the vapour phase, therefore the word “Per-vaporation” is obtained. Unlike reverse osmosis and gas separation, pervaporation is a process that involves a phase change from liquid in the feed to the vapour state in permeate. Therefore, from the energy consumption point of view, pervaporation is preferential when the concentration of targeted species in the feed solution is low.

![Figure 1-10 Schematic diagram of pervaporation process](image)

The history of the pervaporation process originates from the 1910s, when Kober et al. reported the selective permeation of water through a collodion and parchment membrane. The first commercial pervaporation membrane, from Gesellschaft für Trenntechnik (GFT), comprised a thin film of crosslinked polyvinyl alcohol (PVA) coated onto a porous poly(acrylonitrile) (PAN) support. This is used for the dehydration of aqueous ethanol and aqueous isopropanol.

The separation of compounds using pervaporation technology can be classified into three major fields: (i) Dehydration of aqueous–organic mixtures. Pervaporation membranes were initially developed for the dehydration of organic solvents, in this field a hydrophilic polymer such as poly(vinyl alcohol), cellulose, etc. is used to enhance the permeability of water through the membrane. (ii) Removal of volatile organic compounds from aqueous solution. Compared with dehydration,
the removal of dilute organic compounds via pervaporation requires the preferential sorption of the organic component by the membrane. Therefore, an organophilic material is needed to endow excellent affinity between organic compounds and the membrane. (iii) Separation of organic–organic solvent mixture. Organic–organic separation via pervaporation is less developed compared with the former two fields, since there is a lack of robust membrane materials which provide long-term stability in organic solvents. The main applications of organic–organic separation are indicated in Figure 1-11.

![Diagram of major applications of pervaporation process in organic-organic separation](image)

**1.5.2 The solution-diffusion mechanism**

Generally, separation by pervaporation is based on the solution-diffusion mechanism, which is the generally accepted mechanism of mass transport through non-porous selective membranes, such as used for reverse osmosis, pervaporation, and gas separation. It was proposed that the mass transport through the membrane is divided into three consecutive steps: 1) the sorption or dissolution of a component at the upstream surface of the membrane, 2) the diffusion of the component from the surface layer through the membrane, 3) the desorption of the component at the downstream surface of the membrane. (Figure 1-12)
Figure 1-12 Graphical representation of the solution-diffusion mechanism

The mass transport of a component through a membrane has been widely studied. Assuming thermodynamic equilibrium exists at the membrane interface, the mathematical description of permeation in membranes is based on the thermodynamics, that is, the entire driving force which leads to the movement of permeate is the gradient in chemical potential. Therefore, the flux, $J_i$, of component $i$ through the membrane is presented by equation (1)

$$J_i = -L_i \frac{d\mu_i}{dx}$$  \hspace{1cm} (1)

in which $d\mu_i/dx$ is the gradient in chemical potential of component $i$ and $L_i$ is a coefficient of proportionality. This equation simplifies various driving forces, such as gradients in concentration, pressure and temperature, into the gradient in chemical potential. Further, if the driving force is restricted to those generated by concentration and pressure gradients, the chemical potential can be represented by equation (2)

$$d\mu_i = RT \ln(y_i c_i) + v_i dp$$  \hspace{1cm} (2)

in which $y_i$ is the activity coefficient linking concentration with activity, $c_i$ is the molar concentration of component $i$, $v_i$ is the molar volume of component $i$ and $p$ is the pressure.

In a compressible gas phase, molar volume $v_i$ varies with the pressure according to the ideal gas law and integration of equation (2) gives
\[ \mu_i = \mu_i^0 + RT\ln(y_i c_i) + RT\ln \frac{p}{p_i^0} \]  
\[ (3) \]

in which \( \mu_i^0 \) is the chemical potential of pure component \( i \) at reference pressure \( p_i^0 \), where the reference pressure \( p_i^0 \) is defined as the saturation vapor pressure of component \( i \), that is \( p_{i\text{sat}} \). For a compressible gas, equation (3) can be rewritten as

\[ \mu_i = \mu_i^0 + RT\ln(y_i c_i) + RT\ln \frac{p}{p_{i\text{sat}}} \]
\[ (4) \]

In the solution-diffusion model of one component in a solution permeating through membrane, it is suggested that the pressure through the membrane is constant, and the chemical potential gradient through the membrane is only determined by solvent activity, which is illustrated in Figure 1-13.

![Figure 1-13 The driving force gradients of one component in a solution through a membrane, based on the solution-diffusion transport model](image)

Therefore, considering uniform pressure in the membrane and that no pressure gradient exists within the membrane, the gradient in chemical potential is determined by the gradient of solvent activity \( (y_i c_i) \), and according to equations (1) and (2), the component flux can be rewritten as

\[ J_i = -\frac{RTL_i}{c_i} \frac{dc_i}{dx} \]
\[ (5) \]

in which \( RTL_i/c_i \) can be defined as the diffusion coefficient \( D_i \).
\[ J_i = -D_i \frac{dc_i}{dx} \]  

Equation (6) is known as Fick’s law of diffusion. Further integrating over the thickness of the membrane, Equation (6) can be rewritten as

\[ J_i = D_i \frac{(c_{io(m)} - c_{il(m))}}{l} \]  

in which \( l \) is membrane thickness, \( c_{io(m)} \) is the concentration of component \( i \) in the membrane phase \( m \) at the feed interface, \( c_{il(m)} \) is the concentration of component \( i \) in the membrane phase \( m \) at the permeate interface.

### 1.5.3 Application of solution-diffusion model in pervaporation

In the pervaporation process, the driving force of membrane transport is that the vapor pressure of gas on the permeate side is lower than that on the feed liquid side. The feed interface of the membrane is in contact with liquid phase at a pressure higher than the saturation vapor pressure, while the permeate interface is in contact with gas phase at a pressure below the saturation vapor pressure. As mentioned above, in the solution-diffusion mechanism, the pressure within the membrane is the same as the feed pressure, while at the permeate side interface, the pressure drops to a value below the saturation vapor pressure.

At the liquid solution/membrane feed interface, the chemical potential of the feed solution is equilibrated with the chemical potential in the membrane at the same pressure. This can be written as

\[ \mu_i^0 + RT \ln(y_{io}c_{io}) + v_i(p_o - p_{isat}) = \mu_i^0 + RT \ln(y_{io(m)}c_{io(m)}) + v_i(p_o - p_{isat}) \]  

Therefore, the concentration at the feed side interface of the membrane is obtained as

\[ c_{io(m)} = \frac{y_{io}c_{io}}{y_{io(m)}} = K_i c_{io} \]
in which $K_i$ is the liquid-phase sorption coefficient. At the permeate gas/membrane interface, the pressure decreases from $p_o$ in the membrane to $p_l$ in the permeate vapor, the chemical potential in each phase is expressed as

$$\mu_i^0 + RT\ln(y_{il}c_{il}) + RT\ln\frac{p_l}{p_{isat}} = \mu_i^0 + RT\ln(y_{il(m)}c_{il(m)}) + v_i(p_o - p_{isat})$$  \hspace{1cm} (10)

The concentration at the permeate side interface is expressed as

$$c_{il(m)} = \frac{y_{il}}{y_{il(m)}} c_{il} \frac{p_l}{p_{isat}}$$  \hspace{1cm} (11)

The product of $c_{il}p_l$ can be replaced by the partial pressure term $p_{il}$, therefore

$$c_{il(m)} = \frac{y_{il}}{y_{il(m)}} * \frac{p_{il}}{p_{isat}} = K_i^G * p_{il}$$  \hspace{1cm} (12)

in which $K_i^G$ is defined as the gas-phase sorption coefficient. The interconversion of liquid-phase sorption coefficient $K_i$ and gas-phase sorption coefficient $K_i^G$ can be achieved by considering vapor in equilibrium with feed solution, it can be written as

$$\mu_i^0 + RT\ln(y_{io}^L c_{io}^L) + v_i(p_o - p_{isat})$$

$$= \mu_i^0 + RT\ln(y_{io}^G c_{io}^G) + RT\ln\frac{p_o}{p_{isat}}$$  \hspace{1cm} (13)

Therefore,

$$c_{io} = \frac{y_{io}^G}{y_{io}^L * p_{isat}} p_{io}$$  \hspace{1cm} (14)

in which $p_{io}$ is the partial vapor pressure of component $i$ in equilibrium with the feed solution, and the term $y_{io}^L * p_{isat}/y_{io}^G$ is defined as the Henry’s law coefficient, $H_i$. Combining equations (12) and (14) with equation (7) gives

$$J_i = \frac{p^G}{l} (c_{io} * H_i - p_{il})$$  \hspace{1cm} (15)

Since

$$K_i = K_i^G * H_i$$  \hspace{1cm} (16)

$$p_i = p_i^G * H_i$$  \hspace{1cm} (17)
Flux can be rewritten as

$$J_i = \frac{p_i}{l} (c_{io} - \frac{p_{il}}{H_i})$$

(18)

For binary mixtures, the separation of components $i$ and $j$ in the feed solution is realized by the difference of sorption and diffusion parameters of each component. When a pervaporation membrane is contact with feed solution, the thermodynamic equilibrium is formed at the membrane-feed interface, therefore

$$\frac{c_{io(m)}}{c_{io}} = K_i$$

According to Fick’s law,

$$J_i = D_i \frac{(c_{io(m)} - c_{il(m)})}{l} = D_i K_i \frac{(c_{io} - c_{il})}{l} = D_i K_i \frac{\Delta c}{l}$$

(19)

in which both diffusion and sorption coefficient are treated as constant. If the transmembrane concentration $\Delta c$ is considered as the driving force of the membrane process, the permeability of component $i$ through the membrane can be defined as:

$$P_i = D_i K_i$$

(20)

The permeability $P$ is an index which exhibits the intrinsic mass transfer ability through the membrane for component $i$. The separation factor of the membrane for components $i$ and $j$ is defined as

$$\alpha_j^i = \frac{P_i}{P_j} = \frac{D_i}{D_j} \times \frac{K_i}{K_j} = \left(\alpha_j^i\right)_D \times \left(\alpha_j^i\right)_K$$

(21)

Therefore, ideal membrane materials are needed to maximize the difference of these key parameters (the diffusion coefficient $D$, the sorption coefficient $K$, and thus the permeability $P$) in order to optimize the membrane separation behavior.

The solution-diffusion model provides a comprehensive description about pervaporation membrane permeation, and these fundamental equations give a solid theory to interpret the membrane process and the effect of key parameters (such as pressure, concentration and chemical potential) on membrane transport.
1.6 Thin Film Composite (TFC) membranes

In order to develop high-flux pervaporation membranes, many studies focus on the development of asymmetric membrane structures in order to reduce the effective thickness of the membrane. This type of membrane consists of a thin and dense skin layer supported by a macroporous support, combined with non-woven fabrics to provide mechanical strength, which is termed a thin film composite (TFC) membrane. (Figure 1-14) Due to this asymmetric structure type, the permeation flux is significantly improved and extensively applied in the industrial field. The idea of TFC membranes was first suggested by Mulder et al.\textsuperscript{29} in 1983, which was achieved via solution coating of a porous support. Later, the first commercialized TFC membrane was produced by a German company (GFT) in the same year, which was used for the dehydration of ethanol.

![Figure 1-14 Schematic illustration of the structure of a TFC membrane](image)

The porous membrane support is normally prepared via a phase inversion process, in which the homogeneous polymer solution is transferred into a two-phase system, the polymer-rich solid phase is precipitated and generates a dense membrane structure, while the polymer-poor liquid phase generate voids.\textsuperscript{30} It is noteworthy that the support membrane is required to have high porosity in order to minimize the resistance to mass transport. Meanwhile, the pore size should be sufficiently small in order to inhibit the polymer casting solution filling the pore to form an extra layer which reduces the flux.

The fabrication of TFC membranes is composed of two main steps. The first is to cast the porous support membrane as described above; the second is deposition
of a selective dense layer on the surface of the support. In terms of the second step, direct coating of a polymer solution on the support membrane is widely employed to fabricate flat-sheet membranes in various industrial applications. In this process, the polymer (possibly with additives or fillers) is dissolved in a solvent, then the polymer solution is spread on the support and uniformly distributed. On complete evaporation of the solvent, the polymer dense layer will be generated on the surface of the support. Also, some developments have been made based on this process, for example, the mixture of a polymer combined with a cross-linking agent or additives to form a dense layer, followed by post-treatment of the membrane (such as thermal treatment) to achieve a cross-linked polymer structure. 31

1.7 Mixed Matrix Membranes

The widespread application of membrane-based separation processes significantly depends on the permeability, selectivity and stability of the membrane. For the past few decades of development, polymeric membrane materials have seemingly reached the limitation in trade-off between selectivity and permeability. Therefore, for the further improvement of membrane behaviour, the focus of research switches to mixed matrix membranes (MMMs). The concept of mixed matrix membranes was first defined by Kulprathipanja et al.32 in 1988. MMMs comprise an organic polymer as matrix while having nanometer-level inorganic filler incorporated therein. The idea of MMMs was established when inorganic membranes such as zeolite and carbon molecular sieve membranes were found to surpass the upper bound in gas separation and overcome some drawbacks of polymer membranes, such as poor resistance to contaminants, low chemical and thermal stability.33,34 However, the application of inorganic membranes is restricted by their drawbacks, such as high cost and difficulty in membrane fabrication due to fragility. Therefore, mixed matrix membranes are considered as an ideal solution to overcome such problems; the polymer acts as a matrix to provide flexibility while inorganic materials act as nanofillers to enhance the membrane transport performance.
The ideal structure of a mixed matrix membrane is presented in Figure 1-15. As the Figure illustrates, the ideal structure of a membrane consists of two phases, that is a polymer matrix and inorganic nanofiller, without defect and distortion at the polymer-filler interface. However, it is extremely difficult to reach this ideal morphology because of the imperfect filler–polymer adhesion, since the addition of nanofiller particles will influence the properties of the adjacent polymer phase, thus affecting the overall membrane performance. Therefore, nonideal membrane structures with three-phase systems which contain organic–inorganic interface defects have been suggested, that is, besides the polymer and nanofiller particle phase, an interface phase arising from polymer–particle interaction also exists.

![Figure 1-15 Schematic diagram of ideal two-phase MMM structure which consists of polymer matrix and nanofiller](image)

Depending on the polymer–particle adhesion, there are mainly three types of interaction that exist in MMMs, which are presented in Figure 1-16: (1) Interfacial voids between polymer and inorganic fillers. Due to the poor polymer-inorganic nanofiller interaction, the polymer packing is disrupted in the vicinity of the dispersed nanofiller particles and a repulsive force is generated between the two phases, which leads to the formation of nonselective interfacial voids,35,36 (Figure 1-16a) which increases permeability with a loss of selectivity. This kind of morphology is often named as leaky interfacial defects.37 (2) Rigidified polymer layer around the inorganic fillers. If there is excellent interaction between the two phases, the free volume in the polymer adjacent to the nanoparticle is decreased, and the polymer located around the
particle tends to be more dense and rigidified; this kind of morphology is known as polymer rigidification\textsuperscript{38} (Figure 1-16b). Normally, polymer rigidification leads to a dense polymer layer around the particle, which may lead to an improvement of membrane selectivity with the sacrifice of permeability. (3) Particle pore blockage (Figure 1-16c). This kind of morphology is normally caused by the clogging of the pores in porous nanofillers with sorbent, contaminant, or minor components in the feed solution. It can be also classified into total or partial pore blockage, if the pores are completely blocked, the chemical component cannot transfer through the porous particle, therefore no improvement in selectivity is obtained compared with a pristine polymer membrane; if the pores are partially blocked, the permeability is normally decreased, while the selectivity is varied depending on the molecule size and the extent of pore blockage.\textsuperscript{39}

![Figure 1-16 Schematic diagram of nonideal MMM morphologies: (a) interfacial voids, (b) rigidified polymer chain layer, and (c) pore blockage](image)

In MMMs which contain porous nanoparticles, the morphology of pore blockage is normally accompanied with the polymer chain layer rigidification. While the rigidified defect only affects a very thin layer of polymer in the vicinity of the filler, the pore blockage is expected to cause a serious decrease in permeability.\textsuperscript{40} Chung et al.\textsuperscript{39} proposed a zeolite-incorporated MMM permeation model which involves a nonideal three-phase morphology, simultaneously considering the effects of both pore blockage and polymer chain rigidification. It is suggested that MMMs consist of a “pseudo-three phase” system (Figure 1-17). In this system, the third phase
includes the dispersed nanofillers, meanwhile the partial or complete pore blockage caused by the interfacial skin acts as the second pseudo-dispersed phase. The second phase consists of the rigidified polymer layer around the inorganic fillers. Finally, the polymer matrix acts as the first phase. This schematic model has been well developed in terms of a modified three-phase Maxwell model.

![Schematic diagram of nonideal “pseudo-three phase” system morphology of MMMs.](image)

Currently, different models have been developed for the prediction of MMM behaviour, which depend on the membrane morphology. In terms of ideal MMMs with a two-phase structure which consist of inorganic nanofillers and polymer matrix with no defects at the interface, the Maxwell model can predict the effective permeability of a penetrant through the MMM as a function of continuous phase (polymer matrix) and dispersed phase (porous or nonporous nanoparticles) permeability, which is presented as follows

$$P_{\text{MMM}} = P_p \left[ \frac{P_f + 2P_p - 2\Phi_f (P_p - P_f)}{P_f + 2P_p + \Phi_f (P_p - P_f)} \right]$$

where $P_{\text{MMM}}$ is the overall permeability of the mixed matrix membrane, $\Phi_f$ is the volume fraction of the dispersed nanofiller, $P_p$ is the permeability of the polymer matrix and $P_f$ is the permeability of the dispersed nanofiller.
The Maxwell equation was firstly developed in 1873, originally derived for the estimation of the dielectric properties of composite materials, now it has been extensively applied as an effective method for predicting MMM permeability\textsuperscript{41}. It should be noted that the Maxwell model applies at low loadings of spherical particles. When the volume fraction of particles is below 0.2, each particle is considered to be well dispersed in the polymer matrix (Figure 1-18a), and not affected by the adjacent particles\textsuperscript{42}. However, when the volume fraction is higher, some interconnected particles will form and further achieve extended pathways. When the loading is above a certain critical value, almost all the porous fillers are connected, to generate consecutive pathways through the membrane (Figure 1-18b). This value is named as the percolation threshold, and the Maxwell model cannot be applied to calculate the membrane permeability any more. Normally, this percolation threshold depends on the particle size distribution, particle shape, and aggregation status of particles\textsuperscript{1}. The Maxwell model only applies to an ideal morphology (perfect adhesion between polymer matrix and nanoparticle, no defect and distortion to each phase). Therefore, the Maxwell model equation needs further modifications in order to calculate the effective permeability of MMMs with non-ideal morphology\textsuperscript{43,44}, such as in the case of interfacial voids, polymer chain rigidification, and pore blockage.

For mixed matrix membranes, two main types of inorganic nanofillers are normally applied: porous fillers and non-porous fillers. Porous fillers are solid...
nanoparticles containing open pores that correspond to the kinetic diameters of the permeating molecules. Depending on the pore size and structure of the fillers, the separation of permeant molecules with different diameters can be carried out by the selective diffusion through the pores of the nanoparticle. The main representatives of inorganic porous fillers are zeolites,\textsuperscript{45,46} carbon molecular sieves (CMS),\textsuperscript{47,48} metal organic frameworks (MOFs)\textsuperscript{49} and porous silica nanoparticles.\textsuperscript{50} Generally, porous fillers have better selectivity than polymers, and addition of a small amount of porous filler to polymer matrix also leads to significant improvement in its permeability.\textsuperscript{51}

A polymer matrix containing non-porous fillers is another type of mixed matrix membrane. Unlike MMMs with porous fillers, the incorporation of a non-porous filler enhances the permeability (or selectivity) of a membrane by rearranging the effective molecular packing of the polymer chains.\textsuperscript{52,53} It should be noted that a non-porous filler may lead to the generation of nonselective voids at the interface, which improves permeability, but decreases selectivity. Therefore, chemical modification with coupling agents containing organophilic functional groups is suggested, it is expected that excellent interaction between organophilic functional groups on particle and polymer is formed and eliminate the voids to maintain membrane selectivity performance.

In the past few years, many studies reported MMMs with non-porous fillers, such as fumed silica,\textsuperscript{54,35} MgO,\textsuperscript{55} TiO\textsubscript{2}\textsuperscript{56} and graphene.\textsuperscript{53} The results all show that a higher free volume of the polymer is obtained, compared with a pristine polymer membrane, therefore improving the permeability although the fillers are non-porous and impermeable. In this project, our research focuses on the exploration of various non-porous fillers in MMMs, optimizing interface compatibility between the polymer phase and nanoparticles in order to enhance the behaviour of PIM-1 based MMMs.

1.8 Summary of the thesis to be researched

Since PIM-1 is a linear polymer which is solution processable, it is considered as an ideal microporous polymer which can be applied in different kinds
of processing for casting membranes, such as solvent casting and dip-coating. Therefore, in this project, PIM-1 based thin film composite (TFC) membranes and mixed matrix membranes (MMMs) were fabricated and assessed in pervaporation for alcohol recovery.

The first part of the thesis (Chapters 2, 3 and 4) describes the synthesis of PIM-1 polymer and the preparation of membranes for pervaporation. In order to improve the total flux, to meet the demands of industrial application, PIM-1 based thin film composite (TFC) membranes were fabricated. Polyvinylidene fluoride (PVDF) support materials were prepared to explore the influence of the support on the performance of the membrane.

The second part (Chapters 5, 6 and 7) describes the fabrication of PIM-1 based mixed matrix membranes (MMMs). Different types of filler (graphene, Fe₃O₄ particle and organosilicon network) were incorporated into the PIM-1 matrix to illustrate the effects on pervaporation performance of interface voids, which arise from the interaction between the polymer matrix and inorganic nanoparticles.

1.9 References


45–55.


8427–8436.


Chapter 2  Synthesis and Characterization of PIM-1
2.1 Introduction

In this chapter, the representative of linear PIMs, PIM-1, was prepared by a high temperature method. The PIM-1 was characterized by various methods, including Gel Permeation Chromatography (GPC), NMR Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), thermogravimetric analysis (TGA) and surface area measurement via N₂ sorption. The results show that high molar mass PIM-1 polymer can be successfully prepared from the high temperature method. An impressive surface area indicates its microporous property, which shows great potential in the applications of membrane separation and hydrogen storage.

2.1.1 Linear PIMs

PIMs are prepared by the polymerization in which dibenzodioxin linkage is generated base on the double-aromatic nucleophilic substitution mechanism.¹ This reaction enable two covalent bonds formed simultaneously and provide linked group consist of fused ring, therefore generate the consecutive ladder structure polymer with high molecular mass.² Normally, aromatic nucleophilic substitution is achieved if the halide-containing monomer is activated by electron-withdraw substituent (e.g., -F, -CN, etc.)³ A number of PIMs polymer synthesis apply dibenzodioxin linkage reaction, Table 2-1 presents these soluble PIMs, which can be constructed by various monomers to achieve microporous structures with different BET surface area values. Such linear PIMs illustrate that the network structure is not necessary to the formation of microporous materials. A linear polymer whose molecular structure is rigid and contorted can also achieve space-inefficient packing, that is, the restriction of rotational freedom along the polymer backbone guarantees that the macromolecules cannot adjust their conformation and therefore freezes the microporous structure.⁴ Despite this, these PIMs are still soluble in some organic solvents, therefore allowing solution-based characterization, such as average molecular mass by GPC, and
membranes based on these materials can be fabricated via a solvent-casting method.

Table 2-1 Non-network microporous polymers based on dibenzodioxin formation
### 2.1.2 Synthesis of PIM-1

Among the linear PIMs, PIM-1 was considered as one of the most promising due to its impressive surface area and was extensively studied. Currently there are two methods well-developed for the synthesis of PIM-1 polymer. The first method is known as the low temperature method (LTM), which involves the blending of two monomers (TTSBI and TFTPN) in equimolar quantities with potassium carbonate dissolved in anhydrous DMF under inert condition at 65 °C for 72 h. The product was a fluorescent yellow powder which was soluble in polar solvents such as CHCl₃ and THF. In the LTM method, the reaction occurs in relatively dilute condition and therefore is easy to control and suitable to scale up due to the moderate reaction circumstance.

Alternatively, another method, which was developed by Michael Guiver’s group in the Canadian NRC laboratories in 2008, is known as the high temperature method (HTM). This method optimizes reaction conditions and improves efficiency, it was suggested that the rapid stirring of TTSBI and TFTPN (equimolar quantities) in mixture solvent of dimethyl acetamide (DMAc) and toluene instead of DMF at the temperature of 160 °C for 40 minutes. Toluene acts in an important role to facilitate continued stirring, as the mixture becomes viscous with time, therefore improve polymer solubility and drive the reaction to completion. Also, the toluene could favor to remove the water produced in polymerization, which enhance monomer and salt

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Solubility</th>
<th>Name</th>
<th>Surface area (BET, m² g⁻¹)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>A1+B1</td>
<td>THF, CHCl₃</td>
<td>PIM-1</td>
<td>760-850</td>
<td>⁵</td>
</tr>
<tr>
<td>A1+B2</td>
<td>THF</td>
<td>PIM-2</td>
<td>600</td>
<td>⁵</td>
</tr>
<tr>
<td>A1+B3</td>
<td>THF</td>
<td>PIM-3</td>
<td>560</td>
<td>⁵</td>
</tr>
<tr>
<td>A2+B1</td>
<td>THF</td>
<td>PIM-4</td>
<td>440</td>
<td>⁵</td>
</tr>
<tr>
<td>A2+B2</td>
<td>THF</td>
<td>PIM-5</td>
<td>540</td>
<td>⁵</td>
</tr>
<tr>
<td>A3+B2</td>
<td>THF</td>
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<tr>
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<td>⁶</td>
</tr>
<tr>
<td>A1+B5</td>
<td>CHCl₃</td>
<td>PIM-9</td>
<td>661</td>
<td>⁶</td>
</tr>
</tbody>
</table>
compatibility. Both LTM and HTM methods provide PIM-1 with high average molecular mass which guarantee the forming of mechanically robust solvent-casting membrane.

### 2.1.3 Modification of PIM-1

Besides the PIM-1 polymer, several studies also focus on the post-synthesis modification of PIM-1 structure, in which a number of exploration target on the nitrile group substituted by various functional groups to optimize polymer separation and adsorption performance. Table 2-2 illustrates several post-synthesis schemes which were reported in previous literature, these reactions relate to the ethanolamine (EA) and diethanolamine (DEA) modification for CO$_2$/N$_2$ separation and anionic dye Orange II adsorption, $^9$ hydrolysis and metal ion modification for propylene/propane separation, $^{10}$ hydrolysis to prepare ultrafine fibers for removal of dye from water, $^{11}$ hydroxylamine to provide amidoximes, $^{12}$ the reaction with P$_2$S$_5$ to provide thioamides for CO$_2$/N$_2$ separation, $^{13}$ and the reaction of sodium nitride to provide tetrazole functionality. $^{14}$ The modified new PIMs polymer have the potential in the application of gas pair separation, dye adsorption or organic solvent separation.

<table>
<thead>
<tr>
<th>x</th>
<th>R</th>
<th>Reference</th>
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<tr>
<td>diethanolamine (DEA)</td>
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<td>$^9$</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>Functional Group</td>
<td>Page</td>
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<tr>
<td>-----------------------</td>
<td>------------------</td>
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</tr>
<tr>
<td>Zn(NO₃)₂·6H₂O or Mg(NO₃)₂·6H₂O or AgNO₃</td>
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<tr>
<td>NaOH solution or H₂O₂, K₂CO₃</td>
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<tr>
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<tr>
<td>NaN₃/ZnCl₂</td>
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</tr>
</tbody>
</table>

### 2.2 Experimental

#### 2.2.1 Materials

The main solvents, which were purchased from Sigma-Aldrich, are chloroform, 1,4-dioxane, dichloromethane (DCM), methanol (MeOH), ethanol, butanol, dimethylacetamide (DMAc) and toluene.

The materials which were also needed are: 5,5′,6,6′-tetrahydroxy-3,3′,3,3′-tetramethyl-1,1′-spirobisindane (TTSBI, Aldrich), tetrafluoroterephthalonitrile (TFTPN, Apollo Scientific Limited), anhydrous potassium carbonate (K₂CO₃, Fisher Chemical).
2.2.2 Purification of Monomers

5,5′,6,6′-tetrahydroxy-3,3′,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI) needs to be purified before use. 20 g TTSBI was dissolved in MeOH (400 ml) in a beaker. The solution was heated at a temperature of 145 °C by a heating block. When the volume of MeOH evaporated to around 150 ml, the solution gradually became slightly cloudy. Then 300 ml DCM was added slowly into the solution and left overnight. The TTSBI white precipitate was collected by a filter which separates the TTSBI and solvent under vacuum, and the TTSBI was kept in a desiccator overnight to dry.

For the purification of tetrafluoroterephthalonitrile (TFTPN), 400 ml MeOH was added to a flask containing 25 g TFTPN and heated to reflux until the monomer had completely dissolved. The solvent was reduced in volume by evaporation until the solid began to precipitate out. Then the solution was removed from the heat to cool and the precipitate was collected by vacuum filtration. It was washed with a small amount of acetone and dried in a vacuum desiccator to yield TFTPN, which formed as a white crystalline solid.

2.2.3 PIM-1 Synthesis

The PIM-1 was synthesized by the high temperature method. 3.404 g (0.01 mol) TTSBI, 2.001 g (0.01 mol) TFTPN and 4.14 g (0.03 mol) K₂CO₃ were weighed into a 100 ml three-neck flask. Under nitrogen gas, 20 ml DMAc and 10 ml toluene were added into the three-neck flask; a mechanical stirrer was applied to make sure the mixture was dispersed uniformly. Then the synthesis reaction was started at 160°C for 40 min. As the reaction continued, the product become more viscous, and the color also tended to become yellow. When the reaction finished, the final product was precipitated by pouring into methanol and the product was washed with acetone to remove small molecule impurities. After drying in the oven overnight, the PIM-1 was washed in deionized water to remove the solvent in the product, and finally the PIM-1
was washed with 1,4-dioxane to remove the oligomer, and dried in an oven (110°C) overnight. The code of PIM-1 synthesized in this batch is labeled as “LGJ-1” for future use.

### 2.2.4 Characterization of PIM-1

**Gel Permeation Chromatography (GPC)**

The molecular weight distribution of PIM-1 was determined by Gel Permeation Chromatography (GPC) (Viscotek VE 2001), with chloroform as the eluent at a flow rate of 1 ml/min. For the sample preparation, 0.01 g PIM-1 powder was dissolved in 10 ml chloroform, keeping the concentration at 1 mg/ml. After filtration, the PIM-1 solution was injected into a vial, and extracted in the GPC instrument further. Each sample was tested three times. The weight average molecular weight ($M_w$), the number average molecular weight ($M_n$) and the polydispersity (PDI) were analyzed by OmnicSec software.

**$^1$H NMR Spectroscopy**

The PIM-1 structure was determined by NMR Spectroscopy, PIM-1 was firstly dissolved in the CDCl$_3$, and then the sample was transferred into a 5 mm NMR tube through glass wool in a Pasteur pipette. Then the sample was analyzed by a Bruker DRX-400 MHz NMR Spectrometer.

**Fourier Transform Infrared Spectroscopy (FTIR)**

Infrared spectra were recorded on a Thermo Scientific NICOLET iS5 FTIR spectrometer equipped with attenuated total reflectance (ATR) accessory. The background scan was initially operated, samples were directly fixed on the detector to test, each sample was measured for 5 times scanning.
**Thermal Gravimetric Analysis (TGA)**

Thermal gravimetric analysis of PIM-1 was measured by TGA (Mettler Toledo Star@ Systems). PIM-1 powder was loaded onto a platinum pan and heated to 1000 °C under nitrogen atmosphere with heating rate of 10°C/min, the weight loss of sample was recorded as the function of heating temperature.

**Surface Area Measurements**

The surface area testing of PIM-1 was carried out using a Micromeritics ASAP 2020 sorption analyzer. The sample was degassed before measurement at 120°C for 16 h under high vacuum. Then, after cooling, the sample was reweighed, and loaded in the analysis port. Then degassing was operated under the vacuum for 2 h. Nitrogen adsorption/desorption isotherms were measured at 77 K and surface areas determined by multi-point Brunauer-Emmet-Teller (BET) analysis. The free space of the sample tube was recorded after analysis.

**2.3 Results and Discussion**

**2.3.1 The molar mass distribution of PIM-1**

PIM-1 was synthesized by a high temperature method in which the molar ratio of TFTP: TTSBI: K₂CO₃ is 1:1:3, and the volume ratio of DMAc and Toluene is 2:1. The resulting polymer gave a bright yellow fluorescent powder for analysis, the molar mass distribution of PIM-1 was analysis by GPC, the result is presented in Figure 2-1.
GPC results show that the number-average molar mass (\(M_n\)) is 0.6*10^5 Daltons, and the weight-average molar mass (\(M_w\)) is 1.3*10^5 Daltons, which shows that a polymer with decent molar mass was successfully prepared by the high-temperature method.

Polydispersity index (PDI = \(M_w/ M_n\)), which expresses the breadth of the molar mass distribution, is 2.2. It is noteworthy that the polydispersity is slightly higher than data published in literature.\(^{18}\) This is possibly due to the existence of a certain amount of oligomer or low molar mass polymer which decreases the number-average molar mass (\(M_n\)).

**2.3.2 \(^1\)H NMR Spectroscopy of PIM-1**

The \(^1\)H NMR spectrum of PIM-1 is shown in Figure 2-2.
For the NMR spectroscopy analysis, CDCl$_3$ was applied as the solvent for PIM-1. As the $^1$H-NMR spectrum illustrates, there are four different proton environments which correspond to hydrogens of different positions in the PIM-1. The peak which possesses the chemical shift from 1.2 to 1.4 ppm corresponds to the hydrogen on the methyl group, labelled as 1; the two peaks which possess the chemical shift from 2.1 to 2.3 ppm correspond to the hydrogens on methylene group, labelled as 2; the two peaks which possess the chemical shift from 6.3 to 6.4 ppm and from 6.7 to 6.8 ppm correspond to the aromatic hydrogens, labelled as 3 and 4, respectively. Additionally, it can be seen that there are other peaks which are related to the solvent which was used in the polymerization of PIM-1. The peak with chemical shift of 1.56 ppm corresponds to water. Chloroform with the chemical shift of 7.26 ppm is also observed.

2.3.3 FTIR analysis of PIM-1

The FTIR spectrum of PIM-1 is shown in Figure 2-3
As the Figure illustrates, the peaks of nitrile group (\(-\text{CN}\)) and ether linkage (\(-\text{O}-\)) are observed in the FTIR spectrum, where the small peak of 2238 \text{ cm}^{-1} and the sharp peak of 1264 \text{ cm}^{-1} prove the presence of nitrile group and ether linkage, respectively.

### 2.3.4 Thermal Gravimetric Analysis (TGA) of PIM-1

Thermal Gravimetric Analysis (TGA) measurements were conducted to evaluate the thermal stability of PIM-1 polymer. As Figure 2-4 shows, PIM-1 exhibits excellent thermal stability up to 450 \textdegree C, higher temperatures will lead to the degradation of the polymer, which matches well with the data reported by Budd et al.,\textsuperscript{19} this is mainly attributed to the existence of contorted structure (spiro-centre) and fused ring which enhance the rigidity of backbone.
2.3.5 The surface area of PIM-1

The surface area of PIM-1 was determined by nitrogen adsorption/desorption analysis at 77 K. Figure 2-5 shows that an unclosed loop of the desorption curve lies above the adsorption curve. Considerable loading of nitrogen was adsorbed by PIM-1 at a very low relative pressure, this is mainly due to the microporosity property of PIM-1. The BET surface area obtained is approximately 760 m$^2$ g$^{-1}$, which is in the normal range of PIM-1 surface area.
2.4 Conclusions

In this chapter, PIM-1 polymer has been successfully prepared by a high temperature method and characterized. High weight-average molar mass \( (M_w = 1.3*10^5 \text{ Daltons}) \) was obtained by GPC testing, with polydispersity index (PDI = 2.2) which indicates the existence of a small amount of oligomer or low molar mass polymer.

Besides, functional groups in the PIM-1 structures have been fully characterised by \(^1\text{H} \) NMR spectroscopy and FTIR spectroscopy. Thermal stability of PIM-1 was also evaluated using TGA, the existence of a contorted structure (spiro-centre) and fused rings endows PIM-1 with excellent thermal stability which could afford high temperatures up to 450℃.

PIM-1 also exhibits surface area approximately 760 m\(^2\) g\(^{-1}\) via BET analysis, which is attributed to the intrinsic microporosity of the PIM-1 structure.

2.5 Reference


Chapter 3  The Application of a Free Standing PIM-1

Membrane in Pervaporation
3.1 Introduction

In this chapter, a free standing PIM-1 membrane was prepared by the solvent casting method. The membrane was evaluated in pervaporation for butanol recovery from aqueous solution. In order to demonstrate the affinity between a hydrophobic polymer membrane and organic solvents with different polarity, the pervaporation of ethanol/water was also conducted as a comparison.

Additionally, the characterization of the free standing PIM-1 membrane is also carried out, which includes solvent uptake and contact angle testing to illustrate the membrane’s intrinsic hydrophobicity.

3.1.1 Biofuels

Nowadays, with increasing global demand for renewable resources, alternative biofuels production is considered as the main pathway to achieve a sustainable economy. According to the data presented by the U.S. Energy Information Administration, the total world production of biofuel in 2001 was around 54511 m$^3$ day$^{-1}$, which dramatically increased to 304587 m$^3$ day$^{-1}$ in 2012.$^1$ This indicates that biofuels are in high demand in recent years, and have the potential to replace traditional fuels.

Butanol, which is considered as the next generation biofuel, has attracted much attention. Butanol is a 4-carbon alcohol with the molecular formula C$_4$H$_9$OH ($M = 74.12$). Compared with methanol and ethanol, butanol has more superior properties, such as higher energy density, lower volatility, less ignition problems and lower freezing point. The parameters of each fuel are presented in Table 3-1.
Currently, the majority of butanol is produced via a petrochemical route based on propylene oxo synthesis, in which aldehydes from propylene hydroformylation are hydrogenated to yield butanol, therefore, the butanol product is closely related to the propylene market and seriously affected by the cost of oil. (Figure 3-1)

In order to get rid of the dependence of crude oil in the production of butanol, biobutanol, which is considered as an attractive renewable liquid biofuel, attracts much attention. It fits the existing fuel infrastructure and can also be made from more sustainable feedstocks. It is expected that biobutanol is a good candidate as a biofuel, compared with ethanol and bio-diesel, in the biofuel market which is expected to be approximately $247 billion by 2020.\(^2\)

---

**Table 3-1 Comparison of fuels\(^1\)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Petrol</th>
<th>Diesel</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density (MJ L(^{-1}))</td>
<td>32</td>
<td>39-46</td>
<td>16</td>
<td>19.6</td>
<td>27-29.2</td>
</tr>
<tr>
<td>Motor octane number</td>
<td>81-89</td>
<td>-</td>
<td>97-104</td>
<td>102</td>
<td>78</td>
</tr>
<tr>
<td>Boiling point ((^o)C)</td>
<td>27-225</td>
<td>180-343</td>
<td>65</td>
<td>78</td>
<td>117</td>
</tr>
<tr>
<td>Air-fuel ratio</td>
<td>14.6</td>
<td>-</td>
<td>6.5</td>
<td>9.0</td>
<td>11.2</td>
</tr>
<tr>
<td>Density at 20(^o)C (g mL(^{-1}))</td>
<td>0.74-0.8</td>
<td>0.829</td>
<td>0.787</td>
<td>0.785</td>
<td>0.810</td>
</tr>
</tbody>
</table>


3.1.2 The production of butanol via ABE Fermentation

ABE fermentation may be applied to produce renewable biobutanol. It is a process that uses bacteria to produce acetone, butanol and ethanol (ABE). In ABE fermentation, the most commonly used bacteria for biobutanol production are Clostridium strains such as Clostridium acetobutylicum, Clostridium saccharobutylicum and Clostridium beijerinckii. Normally the production ratio of acetone: butanol: ethanol is around 3:6:1, and butanol is the preferred product due to it having the highest value in the chemical market.

ABE fermentation was first developed in the UK in 1912 and it was quickly commercialized for acetone production and spread globally during the first and second world wars. However, in the 1950s, it was gradually ignored since the fuel produced from this method has no cost advantages compared with less expensive petroleum-based chemical synthesis. Recently, as renewable resources attract great attention, interest in the fermentation process has been revived and further developed for the production of biofuel.

However, there are still some problems which restrict the production of butanol by fermentation. One of the main obstacles is the low end-product butanol concentration caused by product inhibition. That is, since the produced butanol is harmful to ABE producing microorganisms, when the butanol concentration in the broth is above an upper limit, it will severely affect the fermentation process, therefore the product inhibition would occur.

For example, in the fermentation process using Clostridium acetobutylicum or C. beijerinckii, the maximum concentration of total solvent obtained (including acetone, butanol and ethanol) is 20 g l\(^{-1}\). This indicates that in 1 liter end product of fermentation broth, at least 980 g water needs to be removed, and in the final 20 g pure solvent, butanol represents 8-13 g. This extremely low concentration of end product restricts the large scale production of butanol. Currently, the main method for butanol recovery is still distillation, which is robust and proven. However it has high energy consumption and is cost infective, therefore, alternative butanol recovery
technology from fermentation broth in more economic processes is extensively studied, such as adsorption, liquid-liquid extraction, gas stripping and pervaporation.\textsuperscript{7}

Adsorption is a process in which a specific chemical component in a solvent or gas mixture is preferentially attached on the surface of an adsorbent.\textsuperscript{1} Previous studies have found that by using the adsorption method, butanol was adsorbed more efficiently compared with ethanol and water on mesoporous carbons.\textsuperscript{8} Despite the high selectivity of butanol, there are still some problems that need to be overcome for this process, such as the difficulty of desorption of organic compounds which were adsorbed before. Additionally, the bacteria which are adsorbed on the adsorbent will decrease the recovery efficiency, especially when the adsorbent needs to be recycled.

Liquid-liquid extraction is an approach to extract dissolved chemical components from a liquid mixture in a certain solvent, by another solvent. Based on this technology, different types of extractants were studied for the removal of butanol from fermentation broth, such as n-decanol and ionic liquids. Although, by means of high performance extractants, excellent butanol/water selectivity can be obtained, extractant fouling is the big issue, which leads to the phase separation and severe contamination of aqueous streams with chemicals.\textsuperscript{9}

Gas stripping is a separation process which is specially for the recovery of volatile products from fermentation. In this process, gas is inflated into the broth and the volatile chemical component is condensed and collected from the condenser. The advantage of this technique is the low cost of operation and also high efficiency of separation. Moreover, only the volatile product is removed from the broth; the reaction intermediates (such as acetic acid and butyric acid) are still in the fermentation broth for recycling. However, in this technology, bubbles which occur in the process of gas stripping lead to foam in a bioreactor, the antifoam agent added is harmful to bacteria and lowers the production of ABE fermentation,\textsuperscript{10} which is the main reason to restrict its application in butanol recovery.

Compared with the process mentioned above, the pervaporation technology is considered as a more promising solution due to the property of energy-efficiency and high productivity. Since in the process of pervaporation, only the chemical
components which permeate through a membrane undergo liquid–vapor phase transition, therefore, from the energy consumption point of view, pervaporation is more economical than energy intensive distillation. Moreover, the pervaporation process can be operated in continuous butanol fermentation, as due to product inhibition effects, the concentration of butanol in the fermentation broth should be maintained at a relatively low level. Therefore, the pervaporation can be combined with fermentation, once the chemical product is formed in the fermentation broth, it can be collected via pervaporation to obtain high and continuous productivity and concentrated butanol permeate stream. The schematic diagram of fermentation combined with butanol recovery by pervaporation process is presented in Figure 3-2.

![Figure 3-2 Schematic diagram of butanol remove from fermentation broth by pervaporation](image)

Therefore, a PV membrane with high flux and selectivity is in large demand for industrial application, and the material for membranes to be used, which is the key point to affect the membrane performance, are extensively studied.

### 3.1.3 Materials for Pervaporation Membranes

The pervaporation for alcohol recovery is to extract an organic compound from aqueous solution, which requires the preferential permeation of larger size organic molecules through the membrane. Therefore, organophilic materials have been extensively studied, since they have high affinity to organic molecules rather than H$_2$O molecules. Currently, the attractive polymer materials which are mainly
applied in organophilic pervaporation include poly(dimethyl-siloxane) (PDMS), poly(1-trimethylsilyl-1-propyne) (PTMSP), poly(ether-block-amide) (PEBA) and PIM-1.

**Polydimethylsiloxane (PDMS)**

Polydimethylsiloxane (PDMS) is a commercialized polymer membrane for pervaporation, which is widely known as silicone rubber. It is an “organic – inorganic” linear elastomeric material, which is shown in Figure 3-3. The backbone of the polymer is mainly composed of Si-O. For the Si-O bond, the bond energy is 451 kJ mol\(^{-1}\), it gives rise to the excellent thermal and chemical stability of the polymer.

![Figure 3-3 The chemical structure of Polydimethylsiloxane (PDMS)](image)

The properties of PDMS are as follows:

1. Excellent adhesion to organics and good hydrophobicity. Since PDMS has low polarity and surface energy, and the majority of organic molecules are low polar or nonpolar as well, this leads to good adhesion between PDMS membrane and organic molecules.

2. Excellent permeability. Since the glass transition temperature of PDMS is low (−123 °C), the polymer chain segments motion tend to move freely and exhibit high flexibility,\(^{11}\) it gives rise to the large free volume which benefits the diffusion of molecules inside the membrane.

3. Excellent heat and cold resistance. The high bond energy of Si-O and Si-C bonds leads to the excellent stability. The relatively low glass transition temperature maintains the rubber form of the polymer. As a consequence, the PDMS membranes can be applied in the range of −60 °C to 150 °C for a long time.
(4) Excellent chemical stability. Si-O and Si-C bonds endow PDMS excellent chemical stability, which can only be broken in the conditions of strong acid and base. Besides, PDMS is also stable in the environment of UV, oxygen and ozone.

(5) Excellent solvent resistance. Organics have good solubility in PDMS, in which swelling always happens, however after the solvent evaporates, the structure of PDMS can recover to its original structure. This can be explained in that in the dissolving process of organics in the membrane, the PDMS segments adjust to the external forces by the rotation of single bonds and the change of segment conformation, after the elimination of the force, the single bond rotation and segment conformation recover. This is the main reason that PDMS presents excellent recovery after swelling by organics.

Currently, PDMS is the main benchmark for hydrophobic pervaporation materials. Much previous work focuses on PDMS-based membranes in the pervaporation of butanol/water, and the reported butanol/water separation factor by PDMS is normally in range of 15 and 50.\textsuperscript{12} However, since PDMS membranes are normally prepared from a crosslinking process, which leads to low flux behavior, the flux of dense PDMS membrane is normally below 1 kg m\(^{-2}\) h\(^{-1}\).\textsuperscript{13} Although decreasing the membrane thickness could enhance the total flux, when the thickness of the membrane is reduced to the sub-micron level, the swelling effect of organic molecules will lead to unstable membrane performance, therefore restricting its industrial application.

**Poly(1-trimethylsilyl-1-propyne) (PTMSP)**

The poly(1-trimethylsilyl-1-propyne) (PTMSP) polymer is a promising material for a butanol-permselective membrane. It is a substituted polyacetylene that combines a rigid backbone chain with a bulky trimethylsilyl side group. The structure is shown in Figure 3-4. The particular configuration restricts the polymer chain packing, resulting in the high free volume and inherent nanoporosity.\textsuperscript{14} Due to its intrinsic nanoporosity, excellent hydrophobicity and glassy nature \((T_g > 300 \, ^\circ\text{C})\),
PTMSP is considered as a candidate in the application of pervaporation, gas separation and vapor permeation.

![Chemical structure of PTMSP](image)

Figure 3-4 The chemical structure of poly(1-trimethylsilyl-1-propyne) (PTMSP)

Although the majority of commercial hydrophobic pervaporation membranes for alcohol recovery are based on PDMS, many studies\(^\text{15,16}\) have confirmed that PTMSP has more superior properties compared with PDMS in both flux and selectivity for alcohol recovery. However the membrane stability is still a big issue, which restricts its industrial application. This is reflected in a gradual decrease in the flux of a PTMSP membrane as the operation time increases in pervaporation, due to the polymer chain relaxation which leads to the shrinking of free volume.

**Poly(ether block amide) (PEBA)**

PEBA is one type of thermoplastic elastomer, which is composed of flexible polyether (PE) segments and rigid polyamide (PA) segments. The structure is shown in Figure 3-5. Depending on the nature and the relative composition of the two segments, PEBA polymers show great potential as membrane materials.\(^\text{17,18}\) For example, PEBA membranes have exhibited excellent extraction ability of aroma compounds from dilute aqueous solution by pervaporation,\(^\text{19}\) and was also shown to be effective for the extraction of phenol from phenolic chemical-containing wastewater.\(^\text{20}\)

![Chemical structure of PEBA](image)

Figure 3-5 The chemical structure of Poly(ether block amide) (PEBA) which consist of polyether (PE) and polyamide (PA) segments

Moreover, PEBA-based membranes have also been evaluated for alcohol recovery. Boddeker \textit{et al.}\(^\text{21}\) studied the pervaporation of isobutanol using PEBA 40
membrane. The results showed that the total flux obtained from PEBA is superior to that of PDMS. Liu et al.\textsuperscript{22} evaluated the application of PEBA2533 in the acetone–butanol–ethanol (ABE) fermentation pervaporation. The membrane permselectivity, which was found to be in the order of n-butanol > acetone > ethanol, demonstrates the potential of using PEBA membranes for ABE extraction from dilute aqueous solutions.

\textbf{PIM-1}

The membrane based on PIM-1, a polymer of intrinsic microporosity, is another type of membrane which draws great attention as a separation membrane. Its high free volume and intrinsic hydrophobic property endows PIM-1 with impressive permeability and decent selectivity, not only in gas separation behavior, but also in application of pervaporation for alcohol recovery. Adymkanov \textit{et al.}\textsuperscript{23} investigated PIM-1 membrane performance in the pervaporation of ethanol from aqueous solution. The results showed competitive flux and decent selectivity. The membrane also exhibited steady performance without showing flux decrease with operating time. Also, a PIM-1 based mixed matrix membrane was developed for improved behavior. Mason \textit{et al.}\textsuperscript{24} investigated the PIM-1/silicalite-1 MMM in the application of ethanol recovery, the incorporation of filler improved the hydrophobic property, therefore enhancing the selectivity of ethanol compared with a fresh PIM-1 membrane.

Additionally, application of a PIM-1 membrane in butanol recovery from aqueous solution was also explored preliminarily. Michal Žák \textit{et al.}\textsuperscript{25} studied the fresh and aged (370 days) PIM-1 membrane performance in pervaporation of butanol/water; due to slow rearrangement of polymer chains, lower flux and higher selectivity were obtained for the aged compared with fresh membrane.

In this section, the pervaporation for butanol recovery from aqueous solution employing a PIM-1 free standing membrane is intensively studied, for demonstrating the affinity between the hydrophobic polymer membrane and organic solvent. The pervaporation of ethanol/water with PIM-1 was also conducted for comparison.
3.2 Experimental

3.2.1 Materials

PIM-1 powder (preparation described in Chapter 2, batch code: LGJ-1, $M_w = 1.3 \times 10^5$ Daltons, PDI = 2.2). Chloroform (amylene stabilized), ethanol and 1-butanol were purchased from Sigma Aldrich.

3.2.2 Solvent casting of free-standing PIM-1 membrane

A free-standing PIM-1 membrane was cast as follows. 0.14 g PIM-1 was dissolved in 10 ml chloroform ($\text{CHCl}_3$) overnight. After filtering through glass wool, the PIM-1 solution was transferred into a glass dish (diameter 6.9 cm). Bubbles on the surface of the PIM-1 solution were removed by gently shaking to make sure that there was no defect in the membrane after formation. Then the glass dish was put in a desiccator without any airflow. The solution was left for 3 days and the solvent evaporated slowly to form a free standing PIM-1 membrane. The thickness of the membrane was determined by a digimatic Micrometer (Mitutoyo), each membrane was tested 10 times in different locations to obtain average membrane thickness and standard deviation.

3.2.3 Pervaporation testing

A batch pervaporation system (Figure 3-6) was constructed in-house, based on a prototype provided by Dr. Pavel Izák, Institute for Chemical Process Fundamentals, Prague, Czech Republic. A circular disk (diameter 1.8 cm) was cut from a membrane sheet, fixed in the membrane cell and sealed with a Viton O-ring. Subsequently, 5 wt.% butanol/water feed solution was prepared and kept at 65 °C by heating with a water bath.

The pervaporation was operated using vacuum as driving force, keeping the pressure on the permeate side at 0.2 mbar. The permeate vapour was cooled by liquid
nitrogen and collected in a trap. Permeate collected during the first hour was discarded, due to the non-equilibrium condition. Then, the pervaporation was run another 2 h. The pervaporation of 5 wt.% ethanol/water followed the same process.

The total flux $J_{\text{total}}$ and separation factor $\beta$ are two main parameters to assess the membrane behavior. Total flux, $J_{\text{total}}$, was calculated using

$$J_{\text{total}} = \frac{m}{At}$$

where $m$ is the mass of permeate collected over time $t$ for a membrane of area $A$. For each type of membrane, measurements were repeated on five membrane discs, to obtain an average and standard deviation.

Separation factors $\beta$ were calculated using

$$\beta = \frac{Y_{\text{butanol}}/Y_{\text{water}}}{X_{\text{butanol}}/X_{\text{water}}}$$

where $Y_{\text{butanol}}/Y_{\text{water}}$ is the weight ratio of butanol to water in the permeate and $X_{\text{butanol}}/X_{\text{water}}$ is the corresponding ratio in the feed.

![Diagram of batch pervaporation apparatus](image)

Figure 3-6 Schematic illustration of batch pervaporation apparatus

Since there is generally a trade-off relationship between productivity and selectivity, the overall performance of a membrane is normally indicated by a pervaporation separation index (PSI).

$$\text{PSI} = J_{\text{total}}(\beta - 1)$$
which is zero if there is no separation, either because there is no flux ($J_{\text{total}} = 0$) or because there is no separation ($\beta = 1$).

### 3.2.4 The determination of butanol concentration

Butanol concentrations in the permeate were determined by gas chromatography (GC). The butanol-water sample was diluted with acetone to form a single liquid phase. Analysis was performed using an Agilent 7820A gas chromatography system with a flame ionization detector, which responds to butanol and acetone, but not to water. The column was a PoraPLOT Q-HT (10 m × 0.32 mm × 20 µm). Helium was used as carrier gas with a constant flow rate of 1.2 mL min$^{-1}$. The ion source was set at a temperature of 190 °C. The oven temperature programming was initially 175 °C, kept isothermal for 2 min, ramped at 15 °C min$^{-1}$ up to 200 °C, and isothermal again at this temperature for 2.5 min. The injection volume was 2 μL, applying a split ratio of 60:1. The scanning time was 6.1 min for each sample.

The concentration of butanol in the diluted sample was determined from the area of the butanol peak using a calibration line from measurements of butanol/acetone/water mixtures of known composition. To determine the calibration line, butanol solutions with a series of concentrations (0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, 2.5 wt%, 3 wt%) were prepared using acetone as solvent, then these samples were run in the GC and the corresponding butanol peak area obtained (Figure 3-7).

![Figure 3-7](image-url) Calibration of gas chromatography system with butanol/acetone/water mixtures of known composition: Area under butanol peak versus wt.% butanol.
Afterwards, in order to determine butanol/acetone/water mixtures with unknown composition, the mixtures were run by GC. According to the area of the butanol peak obtained, combined with the calibration line, the concentration of butanol in the mixtures can be calculated.

### 3.2.5 The determination of ethanol concentration

The concentration of ethanol/water permeate was determined by a refractometer (B+S RFM340+). Firstly, the refractometer was calibrated by the refractometer calibration fluid with a fixed refractive index at 1.39986. A series of ethanol and water mixture solutions with known concentration were prepared, and the refractive index of each sample was tested. From a series of refractive index data, the calibration curve of ethanol concentration and corresponding refractive index result was determined as shown in Figure 3-8.

In the range of ethanol solution concentration from 5% to approximately 30%, the calibration curve of wt. % ethanol and refractive index is nearly a linear equation, which is determined as \( y = 0.0007x + 1.3348 \), which is applied for determination of the weight percent of unknown ethanol solution.

![Figure 3-8 The calibration curve of refractive index versus ethanol concentration.](image)

### 3.2.6 Determination of solvent uptake

The organic solvent uptake of a PIM-1 free standing membrane was
determined by a simple gravimetric test in which the membrane sample was first weighed dry by an analytical balance, then immersed into butanol, 5% butanol solution, ethanol, 5% ethanol solution and water for 10 days respectively. After immersion, the membrane was removed from solvent, using tissue paper to dry the membrane and make sure the solvent on the surface was completely removed. Then the membrane was weighed again. The solvent uptake (SU) was obtained from the following equation:

\[ SU(\%) = \frac{(w_w - w_d)}{w_d} \times 100 \]

where \( w_d \) and \( w_w \) represent the initial weight of the dry membrane and the weight of swollen membrane, respectively.

### 3.2.7 Contact angle testing

Water contact angles of free standing PIM-1 membranes were measured by a Theta optical tensiometer (Biolin Scientific). A droplet of deionized water was placed on a dry membrane sample; the static sessile drop method was applied and data were analyzed by OneAttension software. The angle formed between the liquid and solid interface was determined by a high-resolution camera. Each sample was tested eight times and an average value obtained.

### 3.3 Results and Discussion

#### 3.3.1 The morphology of PIM-1 membrane

A free standing PIM-1 membrane obtained by the solvent casting method is shown in Figure 3-9. The PIM-1 membrane is transparent and has a bright yellow color, this means the lab-made PIM-1 (batch code: LGJ-1, \( M_w = 1.3 \times 10^5 \) Daltons, PDI = 2.2) is qualified to make membranes. The membrane thickness, determined by Micrometer, is \( 26.6 \pm 0.1 \mu \text{m} \).
The free-standing PIM-1 membrane, which was made by solvent casting, was assessed in the pervaporation of 5 wt% ethanol/water and 5 wt% butanol/water mixture. The pervaporation data are given in Table 3-2.

<table>
<thead>
<tr>
<th>Feed solution</th>
<th>5% ethanol solution</th>
<th>5% butanol solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed concentration (wt %)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Flux ($J$) (kg m$^{-2}$ h$^{-1}$)</td>
<td>$0.62 \pm 0.05$</td>
<td>$1.85 \pm 0.07$</td>
</tr>
<tr>
<td>Permeate Concentration (wt %)</td>
<td>$13.7 \pm 1.3$</td>
<td>$50.3 \pm 1.2$</td>
</tr>
<tr>
<td>Separation factor ($\beta$)</td>
<td>$2.7 \pm 0.4$</td>
<td>$19.2 \pm 0.9$</td>
</tr>
<tr>
<td>PSI ($J (\beta-1)$)</td>
<td>$1.04 \pm 0.17$</td>
<td>$32.73 \pm 1.52$</td>
</tr>
</tbody>
</table>

From the data in Table 3-2, it is clear to see that the PIM-1 membrane shows superior performance in the pervaporation of butanol and water, than for ethanol and water. Comparing the flux of pervaporation of ethanol and water, which is around 0.62 kg m$^{-2}$ h$^{-1}$, the flux for butanol and water pervaporation is much higher, around 1.85 kg m$^{-2}$ h$^{-1}$. In terms of the separation factor, the separation performance for butanol/water also overwhelms that of ethanol/water.

The higher total flux and separation factor for butanol recovery can be explained by two following reasons:
(1) The chemical affinity between different organic solvents and the membrane. The water contact angle testing of a PIM-1 membrane (Figure 3-10) gave a contact angle of $86 \pm 2^\circ$. Compared with ethanol, butanol has less polarity due to the increase in the number of carbon atoms, which endows a more hydrophobic property of butanol than ethanol and gives rise to better adsorption for butanol on the surface of the membrane.\(^{26}\)

![Figure 3-10 Contact angle image of free-standing PIM-1 membrane](image)

(2) The interaction between organics-organics and organics-water is another main reason. Normally, for a certain type of solvent, Hansen’s solubility parameter ($\delta$) provides a method which can interpret and predict the adhesion and cohesion property of the solvent on materials or another type of solvent. This concept was developed by Hansen’s group who suggest that the solubility parameter ($\delta$) is affected simultaneously by three types of interaction: $\delta_h$ (the hydrogen bonding interaction), $\delta_p$ (the polarity interaction) and $\delta_d$ (the dispersion interaction).\(^{27}\) The equation is presented as:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

where $\delta$ is Hansen’s total solubility parameter, $\delta_d$ is the dispersive parameter, $\delta_p$ is the polarity parameter and $\delta_h$ is the hydrogen bonding parameter. The value of each parameter was determined by applying Hansen’s Solubility Parameters in Practice (HSPiP) software.\(^{28,29}\) The solubility parameter values for butanol, ethanol and water are presented in Table 3-3.
Table 3-3 Hansen’s solubility parameter values for butanol, ethanol and water

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ_d (MPa^{1/2})</th>
<th>δ_p (MPa^{1/2})</th>
<th>δ_h (MPa^{1/2})</th>
<th>δ (MPa^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>butanol</td>
<td>16.0</td>
<td>5.7</td>
<td>15.8</td>
<td>23.2</td>
</tr>
<tr>
<td>ethanol</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
<td>26.5</td>
</tr>
<tr>
<td>water</td>
<td>15.6</td>
<td>16.0</td>
<td>42.3</td>
<td>47.8</td>
</tr>
</tbody>
</table>

It is widely known that the selectivity is strongly affected by the coupling effect of components in the mixture, to be specific, the extent of interaction of organics with water in the feed.\textsuperscript{31} For a mixture which consists of two components \( A \) and \( B \), the interaction of two components is normally determined by the distance parameter \( \Delta \),\textsuperscript{30,32} which is calculated by Equation (2). The smaller value of the distance parameter \( \Delta \) means a closer affinity, indicating a good interaction between two components.

\[
\Delta_{A-B} = \sqrt{(\delta_{d,A} - \delta_{d,B})^2 + (\delta_{p,A} - \delta_{p,B})^2 + (\delta_{h,A} - \delta_{h,B})^2}
\]  

(2)

Therefore, from the calculation via Equation (2), the distance parameter \( \Delta_{\text{butanol-water}} \) is 28.4 MPa\(^{1/2}\) while the distance parameter \( \Delta_{\text{ethanol-water}} \) is 24.0 MPa\(^{1/2}\), which means water molecules interact with ethanol more strongly than with butanol. This is mainly attributed to the different structure of the butanol molecule, compared with the ethanol molecule, which possesses a large portion of hydroxyl group and thus has a strong hydrogen bonding force with water. The hydroxyl group represents a relatively small portion in a butanol molecule, so even though the hydroxyl portion forms hydrogen bonds to water, these cannot compensate for the significant disruption of the strong hydrogen bonds among the water molecules, required to accommodate the butanol molecules, and results in poor miscibility between butanol and water.\textsuperscript{22}

Comparing the value of \( \Delta_{\text{ethanol-water}} \) with \( \Delta_{\text{butanol-water}} \), it is concluded that water interacts with ethanol more strongly than with butanol, which leads to the high tendency of ethanol forming clusters in the presence of excess water (5 wt% ethanol and 95 wt% water in feed solution), therefore increasing the size of the transmission unit and making the separation of ethanol and water difficult through the membrane.
However, since butanol has weak interaction with water, clustering is weakened, thus the small size of the transmission unit makes the separation of butanol/water easier compared with that of ethanol/water.\textsuperscript{27}

Therefore, since a PIM-1 membrane has superior flux and selectivity performance for butanol recovery compared with ethanol, further research will focus on the improvement of pervaporation in butanol and water mixtures. Additionally, commercial PDMS membrane supplied by Pervatech BV was also tested in our lab to compared with a PIM-1 membrane ubern the same experimental conditions. It was found that the flux of the PDMS membrane is much higher than the PIM-1 membrane (5250 and 1850 g m\(^{-2}\) h\(^{-1}\), respectively). This result is fairly reasonable, since the supported PDMS membrane is normally with a thin PDMS active layer (below 10 μ m) which guarantees the relatively high total flux than a free-standing PIM-1 membrane (26.6 μ m). With regard to separation factor, the PDMS membrane performs less well than the PIM-1 membrane (9.9 and 19.6, respectively), which demonstrates that PIM-1 has better selectivity for butanol/water separation than PDMS, and has the potential to be applied for industrial production.

In order to demonstrate the intrinsic PIM-1 material properties for butanol/water separation, the selectivity \(\alpha\) is needed. The selectivity eliminates the effect of different membrane thickness and different driving force, allowing the systematic studies of the influence of experimental parameters, such as temperature, concentration of feed solution or permeate side pressure. The selectivity of pervaporation \(\alpha\), was determined from the permeability coefficients of butanol and water, \(P_{\text{but}}\) and \(P_{\text{water}}\), respectively

\[
\alpha = \frac{P_{\text{but}}}{P_{\text{water}}} \tag{3}
\]

According to the solution-diffusion model, the permeability coefficient \(P\), or permeance (\(P/l\)), was determined from the following equation

\[
J_l = \frac{P_l(p_{lf} - p_{lp})}{l} \tag{4}
\]
in which \( J_i \) is the flux of component \( i \), \( l \) is the membrane thickness, and \( p_{i,f} \) and \( p_{i,p} \) are the partial pressures of component \( i \) on the feed and permeate side of membrane, respectively. The partial pressure of component \( i \) on the feed side is determined by,

\[
p_{i,f} = x_i \gamma_i p_{i,sat} \tag{5}
\]

in which \( x_i \) is the molar fraction of component \( i \) in the feed solution, \( \gamma_i \) is the activity coefficient of \( i \), \( p_{i,sat} \) is the saturated vapor pressure of \( i \), therefore

\[
\frac{p_i}{l} = \frac{J_i}{p_{i,f} - p_{i,p}} = \frac{J_i}{x_i \gamma_i p_{i,sat} - p_{i,p}} \tag{6}
\]

Since the pressure of the permeate side during pervaporation is extremely low, the term \( p_{i,p} \) can be neglected and the equation is presented as

\[
\frac{p_i}{l} = \frac{J_i}{x_i \gamma_i p_{i,sat}} \tag{7}
\]

In butanol aqueous solution, the activity coefficient of water was equal to 1,\(^{33}\) and the activity coefficient of butanol was determined from the limiting activity coefficient, \( \gamma_B^\infty \), given in Hovaka et al.\(^{34}\) Saturated vapor pressure of component \( i \) \( p_{i,sat} \) can be determined from the Antoine equation,\(^{30}\) which is presented as

\[
\log(p_{i,sat}) = A - \frac{B}{T+C} \tag{8}
\]

in which \( T \) is the temperature (K), and \( A, B \) and \( C \) are Antoine equation constants. Therefore, it can be seen that the saturated vapor pressure changes significantly with the temperature. Antoine constants used for the calculation are listed in Table 3-4.

<table>
<thead>
<tr>
<th>Component</th>
<th>Antoine’s constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>water</td>
<td>5.11564</td>
</tr>
<tr>
<td>butanol</td>
<td>4.6493</td>
</tr>
</tbody>
</table>
Therefore, the selectivity $\alpha$ of PIM-1 membrane in pervaporation of butanol/water operated in 65°C is calculated as

$$\alpha = \frac{P_{\text{but}}}{P_{\text{water}}} = 1.97$$

Žák et al.$^{25}$ have previously reported a study of a free-standing PIM-1 membrane for the removal of butanol from aqueous solution. A fresh PIM-1 membrane with a thickness of 42 $\mu$m was used in pervaporation at 50°C with the feed concentration intervals from 1 to 5 wt%, and the selectivity was found to increase monotonously from 2 to 6 as the feed concentration increases, which is slightly higher than our results. The experiment was conducted under different conditions and the experimental parameters which affect the selectivity results are complicated. They relate to the pervaporation operating temperature (which affects the chemical potential driving force) and concentration of feed solution (which affects the variation of free volume and chain mobility of PIM-1 membrane at the surface side). It is also noteworthy that sometimes the macroscopic property of a membrane, for example, membrane thickness,$^{35}$ also has influence on a membrane material's intrinsic property. As the membrane get thinner, which leads to the higher chemical potential gradient and total flux, therefore the sorption and desorption process may become non-equilibrium, and the solution-diffusion model with constant transport parameters may be not completely fulfilled.$^{25}$

Figure 3-11 illustrates the comparison of membrane performance for pervaporation of butanol/water which relates to the free-standing PIM-1 membrane in this work and other materials from previous literature. It is seen that compared with other membranes, the flux of free-standing PIM-1 membrane (1853 g m$^{-2}$ h$^{-1}$) overwhelms the majority of other membranes, except PTMSP membrane. Fadeev et al.$^{36}$ report that PTMSP free standing membrane (22 $\mu$m) was tested with pervaporation temperature of 70°C using 6 wt% feed solution, both excellent flux (2097 g m$^{-2}$ h$^{-1}$) and separation factor (41) are obtained. In contrast, Borisov et al.$^{15}$ reported PTMSP and PTMSP/PDMSM mixed matrix membranes for butanol
recovery at the PV temperature of 25°C, and a relatively low flux (370 and 330 g m⁻² h⁻¹, respectively) and impressive separation factor (83 and 96, respectively) are obtained, which illustrates that the temperature has a significant effect on membrane performance. Additionally, various PDMS–based commercial membranes were also evaluated. Rozicka et al.³² reported that, compared with Pervatech 030705 and PolyAn, Pervap 4060 which was tested at 25°C had satisfactory flux (1258 g m⁻² h⁻¹) and excellent separation factor (31). Kujawski et al.³⁷ also report PERVAP 1060 and PERVAP 1070 membranes, with the incorporation of ZSM-5 hydrophobic zeolite nanoparticles, PERVAP 1070 exhibit better separation factor than PERVAP 1060 (42 and 29.4, respectively), with the sacrifice of total flux (606 and 1644 g m⁻² h⁻¹, respectively). In summary, PIM-1 membrane exhibits its advantage in the permeability compared with other membranes, while the moderate separation property (β = 19.6) still needs further improvement.

Figure 3-11 Total flux and separation factor for various membranes reported in literature. Symbols: Fadeev et al.³⁶ (PTMSP 70°C), Borisov et al.¹⁵ (PTMSP 25°C), Borisov et al.¹⁵ (PTMSP/PDMDM 25°C), Wang et al.³⁸ (PDMS/ZIF-7 60°C), Mansouri Zadeh et al.³⁹ (PDMS/ceramic hollow fibre, 40°C), Hu et al.⁴⁰ (HBPE-HTPB-PU, 70°C), Kujawski et al.³⁷ (PERVAP 1070, 65°C), Kujawski et al.³⁷ (PERVAP 1060, 65°C), Rozicka et al.³² (PERVAP 4060, 25°C), Rozicka et al.³² (PolyAn, 25°C), Rozicka et al.³² (PERVATECH 030705, 25°C), Biiddeker et al.⁴¹ (PEBA, 50°C), Liu et al.³¹ (PEBA 2533, 23°C).
### 3.3.3 Solvent uptake

The solvent uptake was determined by the gravimetric test. Results for uptake from various mixtures with water, and from pure compounds as a comparison, are given in Table 3-5.

<table>
<thead>
<tr>
<th>Solvent uptake (10 days)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100% butanol</td>
<td>87.1%~93.5%</td>
</tr>
<tr>
<td>5% butanol</td>
<td>42.1%~45.8%</td>
</tr>
<tr>
<td>100% ethanol</td>
<td>35.4%~37.8%</td>
</tr>
<tr>
<td>5% ethanol</td>
<td>6.5%~8.5%</td>
</tr>
<tr>
<td>water</td>
<td>4.3%~5.1%</td>
</tr>
</tbody>
</table>

As Table 3-5 illustrates, the solvent uptake of free-standing PIM-1 membrane in butanol is greater than that in ethanol. Since the contact angle of PIM-1 membrane is around 86°, which is close to hydrophobic property, this leads to good adsorption of butanol molecules in the PIM-1 membrane. However, the problem is that the butanol molecule is also easy to be trapped in the membrane, decreasing the total free volume, which possibly affects the flux of permeate and changes the performance of the membrane. In contrast, due to the high polarity of ethanol, the uptake of ethanol is obviously less than that of butanol, and further for water, the uptake is almost negligible. This reflects that the chemical affinity between membrane materials and solvent indeed influence the mutual adhesion.

### 3.4 Conclusions

In this chapter, PIM-1 membranes are explored in the pervaporation process for alcohol recovery. A free standing PIM-1 membrane was prepared by solvent casting method, then assessed in pervaporation of butanol/water and ethanol/water. The results present promising butanol recovery ability compared with that of ethanol, which is mainly attributed to the excellent affinity between PIM-1 membrane and...
butanol molecules with low polarity, as well as the weak interaction between butanol molecules and water, which was determined by Hansen’s solubility parameters. Therefore, the following research focuses on the improvement of PIM-1 based membranes in the pervaporation of butanol/water separation.

3.5 References


Chapter 4  Recovery of Butanol by Pervaporation using PIM-1/PVDF Thin Film Composite Membranes
4.1 Introduction

In this chapter, PIM-1 based thin film composite (TFC) membranes were developed using a dip coating method. Home-made polyvinylidene fluoride (PVDF) supports were employed in order to increase the flux of permeate and enhance the mechanical strength of the TFC membranes. For the optimization of the support, phosphoric acid, as additive, was incorporated in the dope solution to control the surface pore size and porosity. Several technologies were applied to characterize the TFC membrane, such as the determination of PIM-1 active layer thickness via scanning electron microscopy (SEM), calculation of surface porosity and roughness via Atomic Force Microscopy (AFM), and water contact angle testing.

4.1.1 Background

Although a free standing PIM-1 membrane exhibits great potential in pervaporation for butanol recovery, there are still some problems we need to consider. Firstly, the productivity is one of the main factors which reflects membrane performance. It is expressed in terms of flux. Free standing membranes with high thickness (20-50 μm) normally have comparatively low flux due to high resistance, which restricts the application in industry. Therefore, a very thin membrane is desirable to maximize flux. Secondly, a free standing PIM-1 membrane is too brittle and also tends to form defects during casting of the membrane, and the improvement of mechanical robustness is necessary for practical application. Normally, commercial membranes have an asymmetric structure, with a thin active layer on the surface of a macroporous support. The active layer may be of the same material as the support (integrally skinned), or a different material (thin film composite). In this section, thin film composite (TFC) membranes with a PIM-1 active layer for organophilic pervaporation were intensively studied.

The structure of the expected PIM-1 based TFC membrane is shown in Figure 4-1. The PIM-1 active layer plays the main role of butanol and water
separation. A suitable polymer support can provide mechanical stability to the active layer, meanwhile, improving the separation performance of the entire membrane. Nonwoven fabric only provides mechanical stability to the membrane.

Ideally, the macroporous support in a TFC membrane would merely provide mechanical stability and would not influence the transport properties. However, in practice, the nature of the support may have a profound influence on the performance.

![Figure 4-1 Structure of PIM-1 based TFC membrane](image)

For example, TFC membranes of PIM-1 on polyacrylonitrile (PAN) supports have successfully been applied in organic solvent nanofiltration. However, when PIM-1/PAN TFC membranes were investigated for organophilic pervaporation, the relatively hydrophilic support was found to dominate the behavior. In phenol/water pervaporation, the flux obtained from a PIM-1/PAN TFC membrane was reduced compared with a free-standing membrane, and the separation shifted from organophilic to hydrophilic. This could be attributed to condensation of water within the pores of the hydrophilic PAN support. Moreover, for both phenol/water and butanol/water pervaporation, PIM-1/PAN TFC membranes gave much lower selectivity than those that could be achieved with free-standing PIM-1 membranes. Thus, the development of tailored supports based on a more hydrophobic polymer is in high demand and extensively studied.

4.1.2 PVDF as a support material

Polyvinylidene Fluoride (PVDF) is a semicrystalline polymer, with the chemical structure shown in Figure 4-2. It is an ideal candidate for use as a polymeric support in TFC membranes due to the good mechanical properties and excellent...
chemical resistance. Many previous studies have reported the application of PVDF as the support material for pervaporation membranes with the active layers of PDMS, PDMS/ZIF-7, PEBA, PVA and silica-filled PTMSP. PVDF substrates have been utilized for TFC membranes not only in flat-sheet form, but also in hollow fiber form.

Macroporous polymer supports are normally prepared by a phase-inversion process, most commonly brought about by immersion of a polymer solution in a non-solvent. A previous study also reports that varying the concentration of the polymer solution used to prepare the support will lead to the variation of some support parameters (such as pore size, surface porosity, surface roughness), therefore affecting the total TFC membrane performance. Additionally, a variety of non-solvent additives, such as glycerol, ethylene glycol, polyethylene glycol, lithium chloride, methanol and phosphoric acid, were reported to have been blended into the dope solution to control the surface porosity and pore size distribution of the support. Among these additives, phosphoric acid (PA) can be a particularly effective additive for improving flux due to the impressive pore-inducing ability. Moreover, the finger-like pores can occupy a larger portion on the membrane, which gives rise to larger surface porosity. Therefore, the aim of this section was to develop PIM-1/PVDF TFC membranes for high performance. A series of PVDF supports were prepared, controlling the concentration of PVDF dope solution and the amount of phosphoric acid, in order to illustrate the influence on the properties of the support (such as surface porosity, average pore size and surface roughness). The PIM-1/PVDF TFC membranes were prepared by a dip-coating method. The effect of different PVDF supports on the total performance of TFC membranes will be specifically discussed.
4.2 Experimental

4.2.1 Materials

PIM-1 powder (preparation described in Chapter 2, batch code: LGJ-1, $M_w = 1.3 \times 10^5$ Daltons, PDI = 2.2), polyvinylidene Fluoride (PVDF) (Aldrich, $M_w$ 534,000), phosphoric acid ($\text{H}_3\text{PO}_4$) (Sigma Aldrich), polypropylene (PP) non-woven fabric (Freudenberg Filtration Tech Ltd, Germany).

The main solvents, which were purchased from Sigma-Aldrich, are chloroform (amylene stabilized), 1-butanol, ethanol, dimethylacetamide (DMAC), and formaldehyde (37 wt% in water). A commercial PDMS pervaporation membrane was kindly provided by Pervatech BV (The Netherlands).

4.2.2 Preparation of PVDF supports

For the preparation of PVDF supports, PVDF dope solutions were prepared in DMAC at concentrations of 16, 18, 20 and 22 wt%. The dope solutions were mechanically stirred at 70 °C for 10 h and subsequently left overnight to remove bubbles. Homogeneous dope solutions (normally 25 ml) were cast on PP non-woven fabric at a coating velocity of 0.05 m s$^{-1}$, using an automatic film applicator (Elcometer 4340) (Figure 4-3) with a doctor blade set to a casting gap of 250 μm. After casting, the polymer films were immediately immersed in distilled water at room temperature for 1 h to solidify the support thoroughly. The PVDF supports were stored in dilute formaldehyde solution (1 wt.%) until use, in accordance with the procedure of Claes et al.$^8$ Supports prepared from 16, 18, 20 and 22 wt.% PVDF solution are referred to as PVDF 16, 18, 20 and 22, respectively.

PVDF supports were also fabricated with phosphoric acid (PA) as an additive to control porosity and pore size distribution. PVDF 18 was chosen as benchmark, dope solutions were prepared of 18 wt.% PVDF with 3 and 5 wt.% PA in DMAC, and the above procedure followed. Supports prepared with 3 and 5 wt.% PA are referred to
as PVDF 18-A3 and 18-A5, respectively.

Figure 4-3 Automatic film applicator (Elcometer 4340)

4.2.3 Preparation of PIM-1/PVDF TFC membranes

TFC membranes of PIM-1 on PVDF supports were prepared by dip-coating. Solutions were prepared of PIM-1 in chloroform at concentrations of 2, 3 and 4 wt.%. A PVDF support was dried under vacuum at ambient temperature for 1 h, then a piece (63 × 45 mm) was fixed on a glass slide and the edge sealed with aluminium tape, to ensure only the PVDF-coated side of the support came into contact with PIM-1 solution. A KSV NIMA dip-coater was used to immerse the support vertically into the PIM-1 solution with a constant speed of 100 mm min⁻¹; it was kept immersed for 2 sec, then removed at 100 mm min⁻¹. (Figure 4-4) The membrane was then dried for 10 min in ambient air for solidification to occur. Membranes were stored under ambient conditions, and dried in a vacuum desiccator for 1 h before use.

Figure 4-4 Dip coating method to prepare supported PIM-1 membrane
4.2.4 Membrane characterization

Analysis of morphology

Cross sections of PVDF supports and PIM-1/PVDF TFC membranes were examined by a Field Emission Gun Scanning Electron Microscope (FEG-SEM Philips XL30) at an acceleration voltage of 10 keV. All the membrane sample were frozen in liquid nitrogen, fractured for cross section imaging, then coated with a Au layer (~4 nm) to prevent charging under the electron beam.

Surface characterization of membrane

The surface morphology of PVDF supports was examined by Atomic Force Microscopy (AFM) (Bruker Multimode), with a scanning area of 5 × 5 μm and a scanning rate of 1.0 Hz. 2D surface scanning image, 3D surface structure and roughness parameters were computed automatically using Nanoscope Analysis software. The pore size distribution, average pore size and surface porosity of PVDF supports were determined using ImageJ software. The software converted the AFM 2D surface image to a black and red image, in which red spots represented pores on the support surface; the total red area in a specific area was computed. This was repeated eight times for each sample and an average value obtained.

Contact angle testing

The hydrophobicity of PVDF supports were evaluated by water contact angle using a Theta optical tensiometer (Biolin Scientific). The process was operated as described in Chapter 3.

4.2.5 Pervaporation testing of TFC membrane

The pervaporation of PIM-1/PVDF TFC membranes was operated as described in Chapter 3. Feed solution of 5 wt.% butanol/water was prepared and
Pervaporation was kept at the temperature of 65°C by heating with a water bath. In order to demonstrate the function of the PIM-1 active layer in pervaporation, contrast testing was also operated. Neat PVDF supports were firstly tested in pervaporation. Then PIM-1/PVDF TFC membranes (PVDF 16, 18, 20, 22, 18-A3 and 18-A5 coated in PIM-1 solution of 2, 3 and 4 wt.%, respectively) were assessed via pervaporation under the same conditions.

To investigate the effect of feed temperature on membrane performance, further experiments were undertaken for one membrane (PVDF 18-A3 dip-coated with 2 wt.% PIM-1 solution) at 40 and 50°C to compare with that at 65°C.

An additional experiment was conducted with one membrane (PVDF 18 dip-coated with 4 wt.% PIM-1 solution) to monitor the membrane performance stability in pervaporation over time at 65°C. Pervaporation was firstly run for 1 h to reach equilibrium condition, then the membrane was transferred to a fresh 5 wt.% butanol solution (7.5 g butanol, 142.5 g water), and pervaporation conducted for 5 h, collecting the permeate and a sample of the feed for analysis after each hour.

4.3 Results and Discussion

4.3.1 Structure of PVDF support and TFC membrane

The cross-section structure of a typical support is shown in Figure 4-5. The PVDF support layer is successfully coated on the PP fabric, which clearly exhibits the ideal finger-like structure. It is observed that the smaller pores are on the surface, compared with the pores on the bottom, which is suitable for dip-coating with a PIM-1 solution. The finger structure on the bottom layer is micrometer scale, which guarantees only a little loss of flux. The thickness of the PVDF layer is around 41~45 μm.
Figure 4-5 Cross-section images of PVDF 18 support from scanning electron microscopy at (a) low magnification and (b) high magnification, showing the PVDF layer.

The cross-section structure of a PIM-1/PVDF TFC membrane made by dip-coating is presented in Figure 4-6. The PIM-1 active layer is successfully coated on the PVDF support. Excellent adhesion between PIM-1 and PVDF is obtained. The thicknesses of the PIM-1 active layer in all the TFC membranes have been measured via SEM, and are presented in Table 4-1.

Table 4-1 PIM-1 active layer thickness in TFC membranes using dip-coating with PIM-1 solution concentration of 2.0, 3.0 and 4.0 wt% respectively. Active layer thickness is the mean for at least five measurements and ± indicates the sample standard deviation.

<table>
<thead>
<tr>
<th>PIM-1 conc. (wt.%)</th>
<th>PVDF 16 (μm)</th>
<th>PVDF 18 (μm)</th>
<th>PVDF 18-A3 (μm)</th>
<th>PVDF 18-A5 (μm)</th>
<th>PVDF 20 (μm)</th>
<th>PVDF 22 (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.12 ± 0.11</td>
<td>1.15 ± 0.12</td>
<td>1.01 ± 0.20</td>
<td>0.98 ± 0.17</td>
<td>1.06 ± 0.14</td>
<td>1.24 ± 0.09</td>
</tr>
<tr>
<td>3.0</td>
<td>2.08 ± 0.20</td>
<td>2.23 ± 0.17</td>
<td>2.15 ± 0.16</td>
<td>2.04 ± 0.31</td>
<td>2.12 ± 0.23</td>
<td>2.20 ± 0.24</td>
</tr>
<tr>
<td>4.0</td>
<td>2.95 ± 0.28</td>
<td>2.93 ± 0.24</td>
<td>2.81 ± 0.36</td>
<td>2.72 ± 0.28</td>
<td>2.85 ± 0.29</td>
<td>2.73 ± 0.20</td>
</tr>
</tbody>
</table>
As Table 4-1 illustrates, the factor that affects the thickness of the active layer most strongly is the concentration of PIM-1 solution. The thickness increases as the concentration of PIM-1 solution increases. For the dip-coating conditions employed, the PIM-1 active layer increases from 0.98~1.24 µm for 2 wt% to 2.04~2.23 µm for 3 wt%, reaching 2.72~2.95 µm for 4 wt% PIM-1 solution, regardless of the type of PVDF support.

### 4.3.2 Surface morphology of PVDF supports without additive

The surface morphology of the PVDF supports was investigated by AFM, which was used to scan the surface of the support membranes. The surface images of the supports are shown in Figure 4-7. From the scanning image, a wide range of pore size can be clearly seen on the surface of the support. The average pore sizes and surface porosities calculated by ImageJ software are given in Tables 4-2. The pore size distributions are presented in Figure 4-8.

<table>
<thead>
<tr>
<th>PVDF (wt%)</th>
<th>Average pore size (nm)</th>
<th>Surface porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>68</td>
<td>58</td>
</tr>
<tr>
<td>18</td>
<td>54</td>
<td>52</td>
</tr>
<tr>
<td>20</td>
<td>44</td>
<td>47</td>
</tr>
<tr>
<td>22</td>
<td>28</td>
<td>38</td>
</tr>
</tbody>
</table>

As Table 4-2 illustrates, increasing the PVDF concentration in the dope solution reduces both average pore size and surface porosity in the final support. Actually, average pore size cannot fully reflect the condition of the support surface. From Figure 4-8, it is clear that the pore size distribution is extremely wide for each type of membrane. Although pore sizes in the range of 0~60 nm make up the majority, around 70%, larger pores with sizes greater than 150 nm can still be observed, even pores on the scale of 210~270 nm also exist in PVDF 16.
Figure 4-7 Surface scanning of PVDF supports by AFM (5 μm * 5 μm)
(a) PVDF 16 (b) PVDF 18 (c) PVDF 20 (d) PVDF 22

Figure 4-8 Pore size distributions of PVDF 16, PVDF 18, PVDF 20 and PVDF 22 supports
4.3.3 Surface morphology of PA-PVDF support

Phosphoric acid (PA) additive was applied in the fabrication of PVDF supports to explore the influence of PA on the support performance. PVDF 18 wt% with 3 wt% and 5 wt% PA were prepared and compared with pristine PVDF 18 support, which is referred to as PVDF 18-A3 and PVDF 18-A5, respectively. The surface morphology via AFM scanning is shown in Figure 4-9. Compared with PVDF 18, the incorporation of PA makes the surface pore distribution more uniform. A more dense PVDF surface structure is obtained, especially in PVDF 18-A5.

![Surface scanning by AFM of PVDF supports prepared from 18 wt% PVDF solution (5 μm * 5 μm) (a) without additive, and with phosphoric acid additive at (b) 3 wt.% and (c) 5 wt.%](image)

The average pore sizes and surface porosities, determined by ImageJ software, are presented in Table 4-3. The pore size distributions are presented in Figure 4-10.

Table 4-3 Average pore size and surface porosity of PVDF 18, PVDF 18-A3 and PVDF 18-A5

<table>
<thead>
<tr>
<th>PVDF</th>
<th>Average pore size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>54</td>
<td>52</td>
</tr>
<tr>
<td>18-A3</td>
<td>43</td>
<td>69</td>
</tr>
<tr>
<td>18-A5</td>
<td>25</td>
<td>62</td>
</tr>
</tbody>
</table>

As Table 4-3 illustrates, as the amount of PA additive increases, the average pore size gradually reduces. Meanwhile, it is noteworthy that the porosity of the support shows a dramatic improvement, from 52% to 69% (33% increase) for PVDF18-A3, and to 62% (20% increase) for PVDF18-A5. The results are in line with
the data reported in previous literature. Mansourizadeh et al.\textsuperscript{16} studied the effect of various non-solvent additives on the morphology of PVDF hollow fiber membranes. They reported that 5 wt% phosphoric acid incorporated in 17 wt% PVDF dope solution led to an improvement of surface porosity (24% increase) and narrowing of the mean pore size and pore size distribution. Atchariyawut et al.\textsuperscript{14} also report that for 17 wt% PVDF dope solution with 3 wt% phosphoric acid, using NMP as solvent, the surface porosity is 76%, which is in good agreement with the porosity of PVDF 18-A3 (69%), allowing for the slight difference in dope solution concentration.

These results, combined with the pore size distributions presented in Figure 4-10, lead to the conclusion that the addition of PA effectively narrows the pore size distribution. The number percentage of pores in a range of 1 ~ 30 nm increases dramatically, while the percentage of pores > 60 nm gradually reduces for PVDF 18-A3 and PVDF 18-A5.

The extremely large pores (>180 nm) reduced from 0.2 % in PVDF 18 to 0.07 % in PVDF 18-A3, and in PVDF 18-A5 none are observed. This effectively reduces the risk of leakage through a TFC membrane obtained via dip-coating and leads to formation of a more smooth and defect-free active layer.

Figure 4-10 Pore size distributions of PVDF 18, PVDF 18-A3 and PVDF 18-A5 support
The improvement of pore size distribution and surface porosity can be explained as follows: For PVDF18-A3 support, PA acts as a pore forming-agent, which moderately reduces the pore size, from 54 nm to 43 nm. Additionally, the suitable amount of 3 wt% PA additive enables good compatibility with PVDF polymer using DMAC as solvent. This guarantees full solvent-water exchange in the water coagulation bath, which is possibly the main reason why the porosity increases dramatically from 52% to 69%.

For PVDF18-A5 support, since PA has a strong cross-linking feature,\textsuperscript{14,16} an excessive amount of PA cannot fully dissolve in the PVDF solution. Therefore, partially dissolved PA creates a greater number of smaller pores (which is clear to see in the 0-30 nm range). As result, the average pore size decreases further to 25 nm, which makes the surface more dense. Some PA which does not dissolve in the solution tends to aggregate together, which leads to poor compatibility with PVDF polymer. Therefore one cannot achieve sufficient solvent-water exchange, this is possibly the reason why the porosity reduces from 69% to 63% compared with PVDF 18-A3.

### 4.3.4 Surface roughness and contact angle

Surface roughness is another feature of a support which relates to membrane morphology and hydrophobicity. It is indicated by the roughness parameters: average roughness ($R_a$), peak to valley roughness ($R_z$) and root mean square roughness ($R_q$) from AFM topographical images (Figure 4-11), each value was computed via Nanoscope Analysis software and is tabulated in Table 4-4.

As Table 4-4 illustrates, as the concentration of PVDF dope solution increases, the support surface tends to be more smooth and the surface roughness decreases gradually, which reveals the relationship between surface pore size and roughness. The reduced surface roughness is attributed to smaller pore size tending to create a more smooth and dense surface. This trend has been reported in previous studies.\textsuperscript{10}
Table 4-4 Average pore size, average roughness ($R_a$), peak to valley roughness ($R_z$) and root mean square roughness ($R_q$) of PVDF 16, PVDF 18, PVDF 20 and PVDF 22 supports.

<table>
<thead>
<tr>
<th>PVDF (wt.%)</th>
<th>Average pore size (nm)</th>
<th>$R_a$ (nm)</th>
<th>$R_z$ (nm)</th>
<th>$R_q$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>68</td>
<td>59.4</td>
<td>73.1</td>
<td>56.2</td>
</tr>
<tr>
<td>18</td>
<td>54</td>
<td>52.8</td>
<td>66.3</td>
<td>46.1</td>
</tr>
<tr>
<td>20</td>
<td>44</td>
<td>46.6</td>
<td>56.6</td>
<td>43.7</td>
</tr>
<tr>
<td>22</td>
<td>28</td>
<td>41.5</td>
<td>50.5</td>
<td>30.6</td>
</tr>
</tbody>
</table>

Figure 4-11 3D topographic images of PVDF 16, PVDF 18, PVDF 20 and PVDF 22 support via AFM surface scanning (5 μm * 5 μm)

In order to explore the influence of PVDF dope solution concentration on the hydrophilicity of the support, water contact angle (CA) was also tested. As Figure 4-12 shows, the CA slowly drops as the polymer concentration increases, which indicates that supports fabricated with higher concentration of polymer are more hydrophilic. High concentration polymer tends to form a more dense and smooth surface, which leads to a decrease of roughness. According to the Wenzel model, the hydrophobicity of a membrane will vary correspondingly as the surface roughness, therefore, the surface with high roughness tends to become more hydrophobic, so the support fabricated from low concentration of PVDF dope solution is preferred.
The PA-PVDF support surface roughness was also characterized by AFM analysis and the values are tabulated in Table 4-5, 3D topographic images are presented in Figure 4-13, PVDF 18 without additive is shown as a comparison.

<table>
<thead>
<tr>
<th></th>
<th>Average pore size (nm)</th>
<th>$R_a$ (nm)</th>
<th>$R_z$ (nm)</th>
<th>$R_q$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF 18</td>
<td>54</td>
<td>52.8</td>
<td>66.3</td>
<td>46.1</td>
</tr>
<tr>
<td>PVDF 18-A3</td>
<td>43</td>
<td>47.5</td>
<td>59.5</td>
<td>43.3</td>
</tr>
<tr>
<td>PVDF 18-A5</td>
<td>25</td>
<td>33.8</td>
<td>42.5</td>
<td>28.4</td>
</tr>
</tbody>
</table>

As the data illustrate, the incorporation of PA leads to a reduction of support roughness. Considering the variation of average pore size, this indicates again that the reduction of surface roughness is mainly attributable to a decrease of pore size and narrowing of the pore size distribution, making the surface more dense, which gives
rise to a more smooth surface of the support.

![Water contact angles (CA) of PVDF 18, PVDF18-A3 and PVDF18-A5 supports](image)

Figure 4-14 Water contact angles (CA) of PVDF 18, PVDF18-A3 and PVDF18-A5 supports

Water contact angle (CA) was also tested for PA-PVDF supports (Figure 4-14). As the results show, the incorporation of PA makes the contact angle gradually decrease as expected, this is mainly attributed to the surface having lower roughness.

### 4.3.5 The PV performance of PIM-1/PVDF TFC membranes

PIM-1/PVDF TFC membranes were assessed in pervaporation for butanol and water separation. The PIM-1 TFC membrane PVDF 16 was found to leak during the testing and exhibited extremely high flux and no selectivity at all. According to the previous characterization of PVDF supports, PVDF 16 has the largest average pore size (68 nm) and the widest pore size distribution, it is expected that the large size pores (>210 nm) on the PVDF support leads to the formation of defects in the PIM-1 active layer during dip-coating. That is possibly the main reason why PIM-1 TFC on PVDF 16 did not work in pervaporation.

Moreover, when the fresh PVDF support was assessed in pervaporation as a comparison, the PVDF support did not work in butanol and water separation and completely leaked. PIM-1 TFC membranes with PVDF 18, PVDF 20 and PVDF 22 worked well during the testing. The pervaporation results are shown in Figure 4-15 and Figure 4-16.
The flux performance of PIM-1-based TFC membranes using 2.0, 3.0 and 4.0 wt% PIM-1 solution coated by PVDF 18, PVDF 20 and PVDF 22 support

Figure 4-15 presents the flux performance of TFC membranes. It is clear to see that for the same support, the flux is severely influenced by the concentration of PIM-1 solution. This is mainly attributed to coating by PIM-1 solution with higher concentration tending to increase the active layer thickness, which endows higher resistance to permeation, therefore giving rise to low total flux.

Further, to compare the three types of support coated by the same concentration of PIM-1 solution, it is apparent that the PIM-1 TFC membrane with PVDF 18 exhibits higher flux compared to those with PVDF 20 and PVDF 22. Since, for coating with the same PIM-1 solution, deviations in the active layer thickness are negligible, therefore the flux is mainly determined by the amount of pathways on the support.\textsuperscript{18} As illustrated in Table 4-3, PVDF 18 has the highest surface porosity (around 52\%) of the three types of support, which clearly shows that the surface porosity of the support has a significant influence on the flux performance of the TFC membrane.

The separation factor of PIM-1 TFC membranes is presented in Figure 4-16. The results indicate that as the thickness of the PIM-1 active layer decreases, the separation factor reduces. Ideally, separation factor is only determined by a material’s intrinsic properties regardless of active layer thickness. However, since pervaporation
is a rate-controlled process, in order to achieve higher permeate flux a thinner active layer is needed, then concentration polarization on the boundary layer will occur as the permeate flux increases. That is, due to the retention of less permeable species on the membrane surface, a concentration gradient is formed adjacent to the membrane surface, which acts as a resistance to the feed solution, which will generally lead to a lower extent of separation.\textsuperscript{19,20} The increase in permeation flux intensifies the effect of concentration polarization. Here it is clear to see that for the same type of PVDF support, due to higher flux for a thinner active layer, the separation factor is gradually weakened by concentration polarization. This indicates that in the pervaporation of butanol and water, influence of concentration polarization on membrane performance cannot be ignored.

![Figure 4-16](image)

Figure 4-16 The separation factor of PIM-1-based TFC membranes using 2.0, 3.0 and 4.0 wt% PIM-1 solution coated by PVDF 18, PVDF 20 and PVDF 22 support

For three types of PVDF support coated by the same PIM-1 concentration, it should also be noted that the TFC membrane coated by PVDF 18 has the best selectivity, and that the TFC membrane with PVDF 20 is better than that with PVDF 22. This can be tentatively explained by the surface porosity of support altering the selectivity of the membrane. There are a number of studies observing that both total flux and selectivity relate to the properties of support. Rantenbach \textit{et al.}\textsuperscript{21} studied the removal of phenol from water using a hydrophobic polybutadiene membrane on
polyhydantoine supports with different porosities; it was observed that the supported membranes with high support porosity have high total flux and selectivity. Borges et al.\textsuperscript{22} used ethene-propene-diene rubber (EPDM) as active layer and porous PEI as support for the separation of trichloroethylene from water. The obvious effect of support porosity is observed; it should be noted that low surface porosity of the support leads to high resistance for the organic component, while the water flux was independent of the support. Similarly, in our study, it is found that higher porosity PVDF 18 supports are more hydrophobic than PVDF 20 and 22 and increase the selectivity of the membrane, therefore, the separation performance of the membrane can be improved by optimizing the porosity of the support.

4.3.6 The PV performance of PIM-1/PA-PVDF membranes

For each type of PA-PVDF support membrane (PVDF 18-A3 and PVDF 18-A5), PIM-1 solution (2wt%, 3wt% and 4wt%) was coated to explore the effect of PA additives on TFC membrane PV performance. PVDF 18 is used as a comparison.

The pervaporation performance of PIM-1 coated on PA-PVDF is presented in Figures 4-17 and 4-18.

![Figure 4-17 The flux performance of PIM-1-based TFC membranes using 2.0, 3.0 and 4.0 wt% PIM-1 solution coated by PVDF 18, PVDF 18-A3 and PVDF 18-A5 support](image-url)
The separation factor of PIM-1-based TFC membranes using 2.0, 3.0 and 4.0 wt% PIM-1 solution coated by PVDF 18, PVDF 18-A3 and PVDF 18-A5 support.

As Figures 4-17 and 4-18 show, the membranes coated on PVDF 18-A3 have the best flux and separation factor compared with those on other supports. The incorporation of an optimum amount of PA (3 wt%) improves the surface porosity (up to 69%) and also forms a suitable average pore size (around 43 nm), as well as a more narrow pore size distribution (minimizing the risk of leaking). The enhanced support surface porosity guarantees the higher permeate flux and also a more hydrophobic property of the membrane, which leads to the increase of selectivity.

The membrane with PVDF 18-A5 also has decent PV performance compared with pristine membranes without PA. The porosity is still improved (62%). Possibly due to the smaller average pore size (25 nm), the extremely dense pore slightly hinders the transport of permeate through membrane, which is possibly the reason why flux is decreased a little compared with PVDF 18-A3.

Figure 4-19 illustrates the effects of PIM-1 active layer thickness and of the surface porosity of the support on TFC membrane performance. A plot of the total flux of all supported PIM-1 membranes as a function of the PIM-1 active layer thickness is displayed in Figure 4-19(a). It is clearly demonstrated that for a given support, the total flux, \( J_{\text{total}} \), increases with decreasing thickness of the PIM-1 active layer, which is in line with the Fick’s law of diffusion. Additionally, the membrane
flux performance depends not only on active layer thickness, but also on the support. The primary way in which the support may influence flux is through its surface porosity, as low surface porosity reduces the effective membrane area. This can be taken into account by dividing measured fluxes by the fractional surface porosity, $f_p$, of the support, derived from AFM measurements. The flux may be further normalized for the thickness of the active layer, by multiplying by active layer thickness, $l$. Values of $J_{\text{total}}/f_p$ and $J_{\text{butanol}}/f_p$ are plotted in Figure 4-19(b). It can be seen that different supports give results in very reasonable agreement when the surface porosity is taken into account. However, the thickness-normalised flux decreases with decreasing active layer thickness, over the thickness range 1-3 μm. Thus, although the membranes with the thinnest active layers show the highest fluxes, they are not as high as might be expected on the basis of the performance of TFC membranes with thicker active layers. The thickness-dependence does not extrapolate linearly to very much thicker, free-standing membranes. Extrapolation of the data in Figure 4-19(b) to 27 μm (the thickness of the free-standing PIM-1 membrane in this work) gives a normalised total flux of 147 kg m$^{-2}$ h$^{-1}$ μm, nearly three times higher than the experimental value of 50 kg m$^{-2}$ h$^{-1}$ μm.
The separation factor, $\beta$, increases with increasing butanol flux, normalised for PIM-1 thickness and surface porosity, as can be seen in Figure 4-19(c). The separation factor represents the ability to concentrate up a dilute butanol solution. However, under the conditions of these experiments, butanol fluxes are lower than water fluxes for all the PIM-1/PVDF TFC membranes studied. The high water content of the feed provides a high driving force for water transport. It should be noted that pure water does not pass through a PIM-1 membrane, but water transport is possible when an alcohol is present.$^{23}$ As has been discussed by Rozicka et al.$^{24}$, there is a distinction between the apparent properties of a membrane, in terms of the separation that can be achieved under given conditions, and the intrinsic properties, which relate to the permeabilities of different components through the membrane.

Taking both flux and separation factor into account, Figure 4-19(d) shows that the support has a profound influence on the values of pervaporation separation index ($\text{PSI} = J_{\text{total}}(\beta - 1)$) that are achieved. PVDF18-A3 clearly outperforms the other supports studied here. This demonstrates that optimization of the support is as critical as selection of the active layer in developing composite membranes for applications such as butanol purification.

In conclusion, of all the home-made PVDF-based supports (PVDF 16, 18, 20,
22 and PVDF 18-A3, PVDF 18-A5), PVDF 18-A3 (18 wt% PVDF with 3 wt% of PA) is the best support option, which endows the best performance to PIM-1 TFC membranes. Due to excellent surface porosity (69%) and appropriate average pore size (43 nm), an impressively high flux (9.08 kg m\(^{-2}\) h\(^{-1}\)) is obtained by applying PVDF 18-A3 coated with PIM-1 2 wt% solution, meanwhile maintaining satisfactory separation factor (13.3), and the Pervaporation Separation Index (PSI) reaches 112 kg m\(^{-2}\) h\(^{-1}\) at 65 °C. Moreover, a more uniform pore size distribution is obtained (the proportion of extremely large pores (>180 nm) are reduced from 0.2 % in PVDF 18 to 0.07 % in PVDF 18-A3), this could effectively prevent the formation of defects in the active layer.

For comparison, a free-standing PIM-1 membrane (thickness 27 μm) and composite membrane with a PDMS active layer were tested under identical conditions, with the results shown in Table 4-6. As expected, PIM-1/PVDF TFC membranes gave significantly higher fluxes than the free-standing PIM-1 membrane, albeit with a slight loss of selectivity. Both flux and selectivity were better than for a PDMS composite membrane under the same conditions. Also included in Table 4-6 are representative data from the literature, obtained under a variety of conditions. The fluxes achieved here are higher than for most membranes reported in the literature.
Table 4-6 Butanol/water pervaporation performance of various membranes: active layer thickness, feed temperature, feed composition, total flux ($J_{\text{total}}$), separation factor ($\beta$) and pervaporation separation index (PSI)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Active layer thickness (µm)</th>
<th>Feed temperature (°C)</th>
<th>Feed composition (wt.% butanol)</th>
<th>$J_{\text{total}}$ (kg m$^{-2}$ h$^{-1}$)</th>
<th>$\beta$</th>
<th>PSI (kg m$^{-2}$ h$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1/PVDF 18-A3 (2% PIM-1)</td>
<td>1.0</td>
<td>65</td>
<td>5</td>
<td>9.08</td>
<td>13.3</td>
<td>112</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1 free-standing</td>
<td>27</td>
<td>65</td>
<td>5</td>
<td>1.85</td>
<td>19.6</td>
<td>34</td>
<td>This work</td>
</tr>
<tr>
<td>PDMS supported (Pervatech)</td>
<td>–</td>
<td>65</td>
<td>5</td>
<td>5.25</td>
<td>9.9</td>
<td>47</td>
<td>This work</td>
</tr>
<tr>
<td>PDMS/ceramic hollow fibre</td>
<td>10</td>
<td>40</td>
<td>5</td>
<td>1.28</td>
<td>43</td>
<td>54</td>
<td>This work</td>
</tr>
<tr>
<td>PDMS/PE/brass</td>
<td>65</td>
<td>37</td>
<td>2</td>
<td>0.13</td>
<td>32</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>ZIF-7/PDMS MMM on PVDF</td>
<td>20</td>
<td>60</td>
<td>5</td>
<td>1.69</td>
<td>66</td>
<td>110</td>
<td>5</td>
</tr>
<tr>
<td>PDMS Pervap 4060 (Sulzer)</td>
<td>–</td>
<td>50</td>
<td>5</td>
<td>3.4</td>
<td>39</td>
<td>129</td>
<td>26</td>
</tr>
<tr>
<td>Silica-filled PTMSP/PVDF (VITO 1)</td>
<td>2.4</td>
<td>50</td>
<td>5</td>
<td>9.5</td>
<td>104</td>
<td>978</td>
<td>26</td>
</tr>
<tr>
<td>PTMSP free-standing</td>
<td>22</td>
<td>70</td>
<td>6</td>
<td>2.097</td>
<td>41</td>
<td>84</td>
<td>27</td>
</tr>
<tr>
<td>Surface-modified PVDF</td>
<td>120</td>
<td>50</td>
<td>7.5</td>
<td>4.13</td>
<td>6.4</td>
<td>22</td>
<td>28</td>
</tr>
<tr>
<td>PEBA/ceramic hollow fibre</td>
<td>3.5</td>
<td>40</td>
<td>1</td>
<td>2.01</td>
<td>20</td>
<td>40</td>
<td>29</td>
</tr>
<tr>
<td>Norbornene block copolymer on PAN</td>
<td>1.3</td>
<td>60</td>
<td>1</td>
<td>4.3</td>
<td>21</td>
<td>86</td>
<td>30</td>
</tr>
<tr>
<td>HBPE-HTPB-PU on PAN</td>
<td>31</td>
<td>70</td>
<td>3.42</td>
<td>0.32</td>
<td>10.2</td>
<td>3</td>
<td>31</td>
</tr>
</tbody>
</table>
4.3.7 The effect of feed temperature on PV performance

The PVDF18-A3 coated by 2 wt% PIM-1 solution TFC membrane was operated for pervaporation at 40°C, 50°C and 65°C to explore the effect of temperature on PV performance. The results are presented in Figures 4-20 and 4-21.

As Figure 4-20 illustrates, total flux and partial flux of each component all increase as temperature increases. Sorption and diffusion are the two main steps in the pervaporation process, and temperature has an influence on the solubility and diffusivity. At higher feed temperature, the polymer chains are more flexible and this leads to higher free volume of the polymer matrix for the diffusion of both butanol and water. Therefore, the diffusion rates of individual permeating molecules all increase, which leads to the high flux of each component. A similar trend has also been reported previously.²⁸

![Figure 4-20](https://example.com/figure420.png)

Figure 4-20 The flux performance of TFC membrane using 2 wt% PIM-1 solution coated on PVDF18-A3 with 40°C, 50°C and 65°C feed temperature

Separation factor and PSI are plotted against feed temperature in Figure 4-21. Both separation factor and PSI increase as the temperature increases. Although the partial flux of butanol and water both increase as T increases, the increase of butanol flux is higher than that of water, which leads to the increase of separation factor. From the increase of flux and selectivity with temperature, butanol permeation is more sensitive to temperature increase compared with water permeation.

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²⁸
This could be explained by the Arrhenius relationship\textsuperscript{34}:

\[ J = J_0 \exp(-E_J/RT) \]

Where \( E_J \) is the activation energy of permeation, \( R \) is ideal gas constant \((R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})\) and \( T \) is feed temperature.

In Figure 4-22, the partial fluxes of butanol and water are plotted against reciprocal temperature. It is clear to see that there is a linear relation between flux of each component and the reciprocal of \( T \). According to the equation, the activation energy (\( E_J \)) for permeation of butanol and water can be obtained from the slope of straight line.

\[ y = -2.9432x + 16.926 \quad \text{R}^2 = 0.9825 \]
\[ y = -1.5889x + 13.282 \quad \text{R}^2 = 0.9917 \]

Figure 4-21: The selectivity and PSI of TFC membrane using 2 wt\% PIM-1 solution coated on PVDF18-A3 with 40°C, 50°C and 65°C feed temperature

Figure 4-22: Temperature dependence of permeation fluxes of TFC membrane using 2 wt\% PIM-1 solution coated on PVDF18-A3
Therefore, the activation energy for butanol permeation via calculation is 24.53 kJ mol\(^{-1}\), and the activation energy for water permeation is 13.27 kJ mol\(^{-1}\). Compared with water, the activation energy for butanol permeation is higher, this reflects that the butanol permeation is more sensitive to temperature increase compared with water,\(^{35}\) therefore more flux increase is obtained from butanol, which leads to the increase of separation factor.

**4.3.8 The membrane performance stability**

In order to evaluate the pervaporation performance of TFC membranes for long-term use, an experiment was conducted in which the pervaporation performance was monitored over a 5 h period, sampling the feed and collecting the permeate after each hour. This enables the mass balance to be checked for the pervaporation process. The results are presented in Figure 4-23, As the results illustrate, there are small losses of butanol associated with each sampling step, but on average this is just 1.2\% of the original butanol per step. Within acceptable error, butanol lost from the feed is accounted for in the permeate and in the samples of feed taken for analysis.

![Figure 4-23](image)

Figure 4-23 Dependence on time of fraction of original butanol in the feed (■), fraction permeated (●), fraction in samples of feed taken for analysis (×) and the sum of these (dashed line), for pervaporation of a 5 wt\% 1-butanol aqueous solution at 65°C with a TFC membrane of PVDF 18 dip-coated with 4 wt\% PIM-1 solution.
4.4 Conclusions

In this Chapter, PIM-1 based thin film composite (TFC) membranes were prepared via a dip-coating method. Home-made polyvinylidene fluoride (PVDF) supports were developed in order to increase the flux of permeate and enhance the mechanical strength of the TFC membranes. For the optimization of the support membrane, phosphoric acid (PA), as additive, was incorporated in the dope solution to control the surface pore size and porosity. It is found that the incorporation of PA favors the surface porosity and optimizes the pore size distribution, which could improve both flux and selectivity of the TFC membrane, as well as prevent defects in the active layer. Additionally, long-term operation of a TFC membrane was also tested to evaluate the membrane stability, it is observed that there are slight losses of butanol (around 1.2%) associated with each sampling step, which is in very reasonable error. Compared with a commercial PDMS TFC membrane, the behaviour of PIM-1 TFC membrane is superior not only in total flux, but also in selectivity. Therefore, it is considered as a promising alternative membrane in the pervaporation of butanol.

4.5 References

28, 113–123.
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Chapter 5  The Preparation of PIM-1/Graphene Mixed Matrix Membranes for Pervaporation
5.1 Introduction

In this chapter, PIM-1/Graphene mixed matrix membranes were prepared for butanol/water pervaporation. Homogeneous PIM-1/Graphene solutions were obtained by liquid phase exfoliation of graphite with PIM-1 polymer as stabilizer. Mixed matrix membranes with different loadings of graphene were assessed for butanol/water pervaporation, to evaluate the effect of graphene on pervaporation performance. Several technologies were applied to characterize the membranes, such as Ultraviolet–Visible spectroscopy (UV-Vis), scanning electron microscopy (SEM) and testing of the solvent uptake.

5.1.1 Background

The concept of a mixed matrix membrane (MMM) was first defined by Kulprathipanja et al.\textsuperscript{1} in 1988. It proposes the structure comprised of an organic polymer incorporated with inorganic fillers which have similar compatibility. It combines the advantages of both polymer and inorganic fillers, which endow more superior performance to membranes and is considered as a potential solution to the trade-off relationship between flux and selectivity, which restricts the industrial application of pervaporation.

In the recent development of MMMs for the pervaporation application, different kinds of inorganic nanofiller, such as carbon nanotubes\textsuperscript{2,3}, zeolites\textsuperscript{4,5} and silica particles\textsuperscript{6,7}, were studied to improve the performance of polymeric membranes, such as flux, selectivity or thermal/chemical stability. Some studies report that with the incorporation of an inorganic nanofiller, the flux was normally enhanced while maintaining selectivity, which is explained by the interfacial area created between polymer and filler giving rise to extra free volume.\textsuperscript{8}

In this chapter, graphene is targeted as a nanofiller applied in MMMs to explore the performance improvement in pervaporation. Graphene, the typical 2D material with one-atom-layer thickness, was firstly found by Andre Geim and
Konstantin Novoselov in 2004\textsuperscript{9}. The unique 2D structure endows large specific surface area, high modulus and strength, which has attracted much attention in the academic field.\textsuperscript{10} Currently, graphene and its derivatives, such as graphene oxide (GO), have already been successfully applied in polymer-inorganic composite membranes for various separation processes to improve membrane performance.

Crock \textit{et al.}\textsuperscript{11} report that exfoliated graphite nanoplates mixed with polysulfone (PSF) can dramatically improve the water permeation flux in nanofiltration compared with a pure polysulfone membrane, due to the extra transport cavities created by graphene. Additionally, graphene also works to improve the pervaporation performance of the membrane, \textit{Wang et al.}\textsuperscript{12} studied poly(vinyl alcohol) (PVA)/Graphene composite membranes in the pervaporation of toluene/n-heptane mixtures. They found that the molecular level graphene leads to an enhanced affinity of the membrane to aromatic compounds, therefore improving the membrane selectivity as well as control the degree of swelling. \textit{Yang et al.}\textsuperscript{13} report polydimethyl siloxane (PDMS)/Graphene nanosheet composite membranes in the application of n-octane/thiophene pervaporation. The composite membranes exhibited superior desulfurization performance due to the introduction of graphene optimizing the packing of the polymer matrix and forming extra channels for molecule transport, while maintaining better selectivity due to the $\pi - \pi$ interaction between graphene and thiophene.

Graphene oxide, known as a representative graphene derivative, is normally synthesized from the oxidation of graphite. The Hummer method is a widely applied process for the synthesis of graphene oxide, which involves the oxidation of graphite by strong oxidizing acid (HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}).\textsuperscript{14} The oxidation process endows graphene oxide with functional groups which contain oxygen (Fig. 5-1). This includes $sp^3$-hybridized carbons containing hydroxyl and epoxide functional groups on the top and bottom surfaces, and $sp^2$-hybridized carbons containing carboxylic acid functional groups on the edges. It is naturally hydrophilic and readily disperses in water to form a colloidal suspension.\textsuperscript{15}
Therefore, GO also can be employed as a hydrophilic nanofiller in polymeric/inorganic composite membranes to improve the separation performance. The incorporation of GO will enhance the pure water flux ratio as well as the membrane antifouling ability.

Ganesh et al.\textsuperscript{17} report the incorporation of GO well dispersed in polysulfone (PSF) to form composite membranes for salt rejection. It was found that due to the hydrophilicity of the GO introduced, the pure water flux increased significantly. Wang et al.\textsuperscript{18} studied the effect of GO blended in polyvinylidene fluoride (PVDF) using an immersion phase inversion process to fabricate PVDF/GO composite membranes. They appeared to be more hydrophilic and to have higher pure water fluxes and recovery ratio, meanwhile, the tensile strength and antifouling ability was also enhanced. Zinadini et al.\textsuperscript{19} found that polyethersulfone (PES) containing GO not only improves the water flux due to enhanced hydrophilicity, but also favors the dye removal capability in the nanofiltration of Direct Red 16. These studies all prove that GO has potential as a hydrophilic nanofiller to enhance membrane performance.

Moreover, since various types of functional group exist on graphene oxide, GO can potentially act as a precursor for graphene-based materials. This can be achieved by functionalizing with different kinds of molecule on graphene oxide to endow the special properties we expect. For example, some applications of graphene oxide involve good dispersion in organic solvents, such as for the fabrication of
polymer blended with GO. Therefore, the functionalization of GO from naturally hydrophilic to hydrophobic is the key step. Many studies have been undertaken related to the preparation of functionalized hydrophobic GO. Stankovich et al. first reported the synthesis of chemically modified GO derivatives by the isocyanate treatment of GO, in which the hydroxyl and carboxyl group was treated with organic isocyanates to form carbamate and amide functionalities, respectively. The proposed reactions are shown in Figure 5-2. The modified GO exhibits hydrophobic property and forms stable colloidal dispersions in some organic solvents, such as DMF, NMP and DMSO. Haddon et al. report GO functionalization with octadecylamine (ODA), in which the GO was reacted with SOCl₂ and grafted with aliphatic amine. The modified GO was found to disperse well in THF and 1,2-dichloroethane. Besides chemical modification, GO hydrophobization can also be realized by ionic interaction. Liang et al. report that GO with negative charges (COO⁻) was mixed with amphiphilic molecules carrying positive charge (NR₄⁺), therefore the functionalization of GO was realized through ionic interaction, the hydrophilic head with positive charge adsorbed by GO while the hydrophobic tail was oriented towards the solvent phase. The proposed reactions are shown in Figure 5-3. This treatment makes GO stable in chloroform and prevents aggregation effectively. In summary, the modification of GO makes the graphene derivative disperse well in organic solvents and therefore blend well with polymer to form composite membranes.

Figure 5-2 Proposed reactions in the isocyanate treatment of GO²⁰
Graphene is considered as an ideal candidate for the enhancement of membrane performance. The incorporation of graphene may regulate the structure of the polymer matrix more efficiently and improve the flux and/or selectivity of the membrane. In this chapter, we explore the incorporation of graphene nanofillers in PIM-1 and fabricate PIM-1/Graphene mixed matrix membranes. The membranes were tested for the pervaporation of butanol/water to see if there is any performance improvement.

5.1.2 Liquid Phase Exfoliation of Graphene

Right now, the majority of research focuses on the fabrication of graphene following the route: (1) The oxidation of graphite to obtain graphene oxide (GO), then (2) the reduction of GO to obtain reduced graphene oxide (rGO). (Figure 5-4) This method is well developed and also easy for large-scale production.

![Figure 5-4 Chemical structure of graphene-based materials (a) Graphene (b) graphene oxide (c) reduced graphene oxide](image)
However, due to the rGO suffering from the oxidation of graphite and then reduction, the reduction process cannot remove all the functional groups on the sheet, and structural defects on the graphene also exist.\textsuperscript{23} These defects may disrupt the properties of graphene, lowering its original hydrophobicity, further affecting the performance of graphene-based membranes. Moreover, the process of rGO which is made by oxidation, exfoliation and reduction involves harsh and non-environmentally friendly chemistry. Therefore, it is necessary to explore more optimized and environmental methods to exfoliate graphene.

Therefore, other methods of graphene fabrication are being explored extensively. The liquid phase exfoliation (LPE) process draws attention due to its simple treatment of graphite in moderate conditions. In this procedure, graphite is exfoliated in the liquid environment by employing ultrasound to extract graphene. The liquid phase exfoliation normally includes three steps: (1) The dispersion of graphite in solvent, (2) the exfoliation by ultrasonication (3) purification by centrifuge.\textsuperscript{24} The form of graphene is achieved by shear force and cavitation, which acts on bulk materials to induce exfoliation.\textsuperscript{25} When the exfoliation finishes, the interaction between graphene and solvent needs to counteract the inter-sheet attractive force. An ideal candidate solvent is expected to minimize the interfacial tension between graphene and the liquid.

Previous studies have confirmed that solvents with surface tension around 40 mJ m\textsuperscript{2} are the ideal solvents which could minimize the interfacial tension between graphene and solvent,\textsuperscript{36} which corresponds to solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) and ortho-dichlorobenzene (o-DCB), however, these solvents are toxic and harmful to the human body. Additionally, their high boiling point (NMP 203°C, DMF 154°C, o-DCB 181°C) restricts their application, since the solvent is difficult to evaporate at normal temperatures, therefore limiting the materials fabrication. For the low boiling point solvents which are normally used, such as water, chloroform and ethanol, their surface tensions do not match well with that of graphene, therefore they are difficult to be directly used as the solvent for graphene exfoliation.
Aiming to improve the graphene exfoliation in different kinds of solvent, recent studies focus on surfactant assisted exfoliation. This involves small organic molecule surfactants which facilitate the graphite exfoliation. Due to the high adsorption energy, the surfactants tend to adsorb on the basal plane of graphene and make it possible to stabilize the graphene in various kinds of solvent, such as water and organic solvents.\textsuperscript{27}

For graphene dispersion in aqueous solution, small molecule surfactants such as pyrene derivatives\textsuperscript{28,29}, perylene-based bolaamphiphiles (PBBA)\textsuperscript{30,31} and coronene tetra-carboxylic acid (CTCA)\textsuperscript{32} are reported to be employed for the promotion of graphene well dispersed in aqueous solution.

For graphene dispersion in organic solvents, CTAB\textsuperscript{33}, porphyrins\textsuperscript{34} and quinquethiophene-terminated PEG (5TN-PEG)\textsuperscript{24} are reported to be applied as surfactants in the exfoliation of graphite in organic solvent media.

However, although it is confirmed that with the aid of small molecule surfactants it is possible to exfoliate graphite into graphene in some organic solvents, this should be associated with the practical experiment situation. In our project, the main aim is to fabricate PIM-1/graphene mixed matrix membranes for the pervaporation of butanol/water and explore the effects of graphene nanofiller on the performance of the membrane. However, if small molecule surfactants are added as dispersants, they still exist in the mixed matrix membrane when fabricating the membrane by solvent casting and possibly block the cavities in the membrane and, as a result, decrease pervaporation performance. Therefore, based on this thinking, the incorporation of extra small molecule surfactants in solvent is not our first choice.

5.1.3 Liquid Phase Exfoliation of Graphene with Polymer as Surfactant

Some recent studies report that graphite can be exfoliated in the presence of polymer. Coleman \textit{et al.}\textsuperscript{35} explored the different types of polymer applied as surfactants in the exfoliation of graphite. He proposed the model in which when the
Hildebrand solubility parameter of polymer and solvent are similar to that of the graphene nanosheet, the polymer is effective as a surfactant in the exfoliation.

Xu et al.\textsuperscript{36} successfully prepared graphene dispersions with high concentration in low boiling point organic solvents (CHCl\textsubscript{3} and THF) with the assistance of hyperbranched polyethylene (HBPE). The distribution of 2~4 layers of graphene shows that HBPE acts as an excellent surfactant which can be employed in exfoliation of graphite.

Liang et al.\textsuperscript{37} reports that graphene exfoliation is successfully achieved in ethanol solvent with the addition of stabilizer polymer, ethyl cellulose (EC). The moderate process is used at room temperature with centrifugation-free solvent exchange with high yield of 1 mg/ml of graphene dispersion.

Based on previous studies, it is expected that the graphene prepared from polymer-assisted LPE of graphite is superior to that from small molecule-assisted LPE, not only in final graphene concentration, but also in the mutual combination between polymer and graphene. Moreover, the graphene which is exfoliated in the presence of polymer makes a good foundation to fabricate mixed matrix membranes. Therefore, PIM-1 polymer can be considered as a surfactant for the exfoliation of graphene using LPE method without other chemicals introduced.

The previous work in our group by Alhumayri\textsuperscript{38,39} has confirmed that graphene exfoliation in PIM-1 solution can be achieved with the method of addition of graphite flakes to PIM-1 solution, followed by treatment by sonication. The mixture exhibits homogeneous dispersion and high concentration of graphene is obtained. Mixed matrix membranes were prepared by solvent casting and the performance assessed in gas separation. In this chapter, we follow the same method of graphene exfoliation in PIM-1 solution, and evaluate the performance of PIM-1/graphene membranes in pervaporation of butanol/water.
5.2 Experimental

5.2.1 Materials

PIM-1 powder (preparation described in Chapter 2, batch code: LGJ-1, $M_w = 1.3 \times 10^5$ Daltons, $PDI = 2.2$). Graphite flakes (Sigma-Aldrich), Chloroform (amylene stabilized) and 1-butanol were purchased from Sigma-Aldrich.

5.2.2 Preparation of PIM-1/Graphene dispersion via LPE

The preparation of PIM-1/graphene dispersions via LPE follows Althumayri’s method\textsuperscript{38}: 100 ml PIM-1 solution ($C_{PIM-1} = 14$ mg/ml) was prepared using chloroform as solvent, then 0.6 g graphite flake was added to the PIM-1 solution (keeping the initial graphite concentration $C_{Graphite} = 6$ mg/ml), then the bottle with the PIM-1/graphite mixture was sealed tightly by aluminum foil and treated by sonication.

The sonication was operated in the ultrasonic water bath (Elmasonic P70H, 220 W ultrasonic power, 37 kHz ultrasonic frequency) for 84 h. The bath was equipped with an external pipe for water recycling in order to keep the water bath at room temperature and prevent overheating.

After the sonication, the bottle with the treated sample was stood for 30 min without any movement before centrifuging. Centrifuging was carried out using an Eppendorf Centrifuge 5804. Firstly, 80 ml supernatant was transferred into 2 disposable polypropylene tubes (40 ml each), then the tubes were placed into the centrifuge at symmetric positions. Based on previous experiments, the centrifuge was operated with a speed of 10000 rpm for 20 min. Once finished, the tube with 40 ml solution was stood for 10 min, then 25 ml supernatant (in total 50 ml) was collected for future experiments.
5.2.3 Determination of Graphene Concentration in Dispersion

The graphene concentration in PIM-1/graphene dispersions was determined by UV-Vis spectroscopy, The Beer-Lambert law was applied to calculate the graphene concentration in PIM-1/graphene dispersion.

\[ A = \varepsilon \times C \times l \]

Where \( A \) is absorbance which is determined by UV-Vis spectroscopy, \( C \) (mg ml\(^{-1}\)) is the concentration, \( l \) is the cuvette pathway length (normally 1 cm), \( \varepsilon \) (mg ml\(^{-1}\) cm\(^{-1}\)) is the extinction coefficient, the extinction coefficient of graphene was determined by Coleman as 36.2 mg ml\(^{-1}\) cm\(^{-1}\) at 660 nm.\(^{40}\) Therefore, \( C_{\text{graphene}} \) can be determined.

5.2.4 Preparation and Characterization of PIM-1/Graphene Mixed Matrix Membranes

The PIM-1/graphene MMMs with different graphene loadings were prepared by the solvent casting method as described in Chapter 3. According to the desired loading of graphene in the MMM, the original PIM-1/graphene dispersion was diluted by pure PIM-1 solution (\( C_{\text{PIM-1}} = 14 \) mg/ml) to achieve the expected graphene concentration while maintaining the concentration of PIM-1 at 14 mg/ml. For each membrane, 10 ml PIM-1/graphene dispersion was used for membrane casting.

The morphology of PIM-1/graphene MMMs was examined using SEM. The cross section of membranes with different loadings of graphene was tested as described in Chapter 2.

PIM-1/graphene MMMs were also tested for the degree of swelling by butanol for 10 days as described in Chapter 2. Free-standing PIM-1 was also tested as a comparison.
5.3 Results and discussion

5.3.1 The Dispersion of PIM-1/Graphene Mixture via LPE

As Figure 5-5 shows, the PIM-1/graphene mixtures produced by Althumayri’s LPE method exhibit homogeneous dispersion of graphene in PIM-1 solution. The dispersions are extremely stable and no sediment is found even two years after the sample was prepared.

![Image of PIM-1/graphene dispersions with a series of loadings of graphene](image)

The concentration of graphene in the original PIM-1/graphene dispersion was determined via UV-Vis spectroscopy at a wavelength of 660 nm, as Figure 5-6 illustrates. For pure PIM-1 solution, as comparison, no absorbance at 660 nm was found.

![Figure 5-6 UV-spectroscopy of original PIM-1/graphene dispersion by Althumayri’s LPE method and pure PIM-1 solution](image)
According to the absorbance at 660 nm, calculated from the Beer-Lambert law, the concentration of graphene in original PIM-1/graphene dispersion is 0.1 mg/ml.

When the original dispersion was diluted by pure PIM-1 solution or chloroform, the dispersion still exhibits a homogenous state and no aggregation occurs. This provides a good foundation for membrane casting with different graphene loadings.

In Althumayri’s previous work, a control sample was also made by addition of graphite to chloroform (without PIM-1 polymer as stabilizer), which was also treated by sonication and centrifugation with the same procedure. The results show poor dispersion of graphene and the majority of sediment occurring in the bottle, which confirms chloroform is a poor solvent for graphene. It also shows that PIM-1 acts as a polymeric stabilizer, giving excellent dispersion of graphene in chloroform.

It is important to clarify the mechanism of polymer stabilization of graphene dispersions. It is well known that polymer stabilization of colloids depends on the steric stabilization mechanism, that is the polymer chains have one part attached to the colloid while the other part protrudes into the solvent. When two adjacent polymer-coated colloidal particles encounter each other, the polymer chains in the solvent will repel each other and stabilize the colloid to prevent aggregation. Here in the system of PIM-1 polymer, graphene and solvent, since PIM-1 is an aromatic polymer, it is possible that noncovalent interactions (\(\pi-\pi\) interactions) between PIM-1 and graphene exists, which favor PIM-1 attaching to the basal plane of graphene to prevent the graphene from restacking and to maintain their stable dispersion in PIM-1 solution.

Therefore, combining the above mechanisms, it is concluded that part of the PIM-1 is attached on the graphene basal plane at a certain number of sites, while some of the PIM-1 chain protrudes into the solvent to maintain steric stabilization in solution.

Actually, for the graphene surface, there is the competition between polymer and solvent; the introduction of PIM-1 stabilizes the graphene flake to a large degree
by the interaction between graphene and PIM-1. There are two types of interaction that exist in the system, the polymer-graphene interaction which leads to the adsorption; and the polymer-solvent interaction which leads to desorption; the two opposite interactions achieve dynamic equilibrium, and reach the steady state of graphene flake in solvent with the aid of polymer to form good dispersions.\(^3\)\(^6\)

### 5.3.2 Raman Spectroscopy

Raman spectroscopy is an important method which is used to characterize graphene samples. It can determine the number of layers, the flake defects and stacking order. The Raman spectrum of graphene normally consists of three main bands: the D band (around 1325 cm\(^{-1}\)), the G band (around 1580 cm\(^{-1}\)) and the 2D band (around 2650 cm\(^{-1}\)). The D band corresponds to the existence of defects, which is possibly attributed to the edges or functionality of graphene flakes. The G band corresponds to vibration of the lattice of sp\(^2\) carbon atoms. The 2D band is the second order of D, which is related to the dispersion of two phonons. Figure 5-7 presents the Raman spectra of graphite, few layer graphene (2~10 layers) and single layer graphene in NMP dispersion, which are provided by our collaborator Yuyoung Shin. For the D and G peaks, the intensity decreases as the number of layers increase. Moreover, the D peak was also influenced by the defects which derive from the basal-plane or from the flake edge.

In Raman spectra, 2D peak symmetry provides more information about the sample. Compared with graphite flake, single layer and few layer graphene exhibit more symmetric 2D peaks, and for the single layer graphene the peak is more sharp and narrow. For the few layer graphene, a wider peak is observed. However, few layer graphene with regular stacking (known as A-B stacking) exhibits an asymmetric 2D peak. The 2D peak can be fitted with a Lorentzian lineshape and the coefficient of determination (R\(^2\)) obtained.
Figure 5-7 Raman spectra of samples obtained from liquid phase exfoliation of graphite in NMP, presents the differences in the shape of the each peak for single-layer graphene, few-layer graphene and graphite. Data was provided by Yuyoung Shin.

With regard to the Raman characterization of PIM-1/graphene dispersions, the sample was characterized by our collaborator Yuyoung Shin et al.\textsuperscript{43} Results are presented in Figure 5-8 (a). Due to the strong photoluminescence of PIM-1 polymer, the signals of the D peak and G peak overlap with that of PIM-1, which disturbs the analysis of Raman spectroscopy. However, in the 2D peak position, no signal is found for pure PIM-1. Therefore, for the sample, only the 2D peak signal can be used for the analysis of PIM-1/graphene dispersion samples. Here the asymmetric shape of the 2D peak in the sample indicates that few layer graphene with random stacking order exists in the sample.

Figure 5-8 (a) Raman spectra of pure PIM-1 and PIM-1/graphene sample, (b) Lorentzian fitting of the 2D peak in PIM-1/graphene sample, data were provided by Yuyoung Shin.
The Lorentzian fit was also operated to calculate the coefficient of determination $R^2$ by Shin in Figure 5-8 (b). The result indicates that no single layer graphene was found in the sample.

Therefore, it is concluded that with the aid of PIM-1 polymer as stabilizer, well dispersed and high concentration of few layer sheets in chloroform can be achieved. However, it is still difficult to obtain single layer graphene in this solvent system, the majority of sheets exist in the form of few layer graphene, and restacked when the dispersion has dried.

5.3.3 Morphology of PIM-1/Graphene MMMs

A series of PIM-1/Graphene MMMs was prepared by the solvent casting method. By diluting a PIM-1/graphene dispersion with PIM-1 solution ($C_{PIM-1} = 14$ mg/ml), PIM-1/Graphene MMMs with different graphene wt% (0.009, 0.018, 0.035, 0.07, 0.14, 0.28, 0.42, 0.57, 0.7) were prepared, which are presented in Figure 5-9. It is clear to see that as the loading of graphene increases in the MMM, the color of the membrane changes from bright yellow to dark brown. All the membranes exhibit uniform dispersion and no obvious sheet aggregates were found, even at high loading of graphene in the MMM.

![Figure 5-9 PIM-1/Graphene MMMs with a series of graphene loadings](image)

Scanning electron microscopy (SEM) was applied to see the morphology of cross sections of MMMs, which is presented in Figure 5-10. Compared with the smooth morphology of a pristine PIM-1 membrane, Figure 5-10(a), it is obvious that
the incorporation of graphene nanofiller in the polymer matrix strongly affects the morphology of the membrane. The cross sections exhibit more roughness as the loading of graphene increases. Nevertheless, the membrane still presents homogeneous dispersion of graphene in the polymer matrix, and no obvious aggregated graphene was found in the matrix, which provides a good foundation for the application of MMMs.

Figure 5-10 Cross section SEM images of PIM-1/graphene MMMs with different graphene loading
(a) pristine PIM-1 (b) 0.035 wt% (c) 0.07 wt% (d) 0.14 wt% (e) 0.42 wt% (f) 0.7 wt%.
5.3.4 Pervaporation with PIM-1/Graphene MMMs

PIM-1/graphene MMMs with different graphene loadings were tested in the pervaporation of 5% butanol and water with the temperature of 65°C, following the procedure as described in Chapter 3. The fresh freestanding PIM-1 membrane was also tested as a comparison. The results are shown in Figure 5-11.

![Figure 5-11](image)

Figure 5-11 Flux and separation factor of PIM-1/graphene MMMs with a series of graphene loadings in pervaporation of butanol/water with 5 wt% feed solution at a temperature of 65°C

For a non-porous inorganic filler in a mixed matrix membrane, normally there are two pathways for the molecular transfer: (1) through the polymer matrix, (2) through the interface generated between polymer and filler. If there is excellent compatibility between polymer matrix and filler, a selective interface is formed at the molecular scale, which could maintain or improve the selectivity; if there is poor compatibility between polymer and filler, a non-selective void will form, which will increase flux at the expense of selectivity.

In this study, it can be seen from Figure 5-11 that the loading of a certain amount of graphene improves the flux while maintaining the selectivity, which illustrates that there is good compatibility between PIM-1 polymer and graphene,
possibly due to π - π interactions. A small amount of graphene loading (around 0.018 wt%) increases the flux from 1.83 kg m\(^{-2}\) h\(^{-1}\) (pristine PIM-1 membrane) to 2.03 kg m\(^{-2}\) h\(^{-1}\); approximately 11% flux improvement is obtained. As seen in the SEM images of MMM cross sections (Fig. 5-10), the MMM with 0.018 wt% loading has well dispersed graphene filler in the PIM-1 matrix, which possibly leads to optimization of PIM-1 polymer packing, extra free volume is obtained due to the formation of an interfacial area between polymer and filler, meanwhile the interface for butanol/water is selective which maintains the separation factor. At 0.018 wt% loading graphene the separation factor (18.5) is in the same level compared with that of pristine PIM-1 membrane (19.4).

As the graphene loading continually increases, the extra graphene nanofiller tends to restack, or even agglomerate, which possibly squeezes the interface area and blocks the interfacial channels. Additionally, since graphene flake is considered as a barrier, extra graphene may also hinder the permeate transfer through the polymer matrix. It is clear that as the loading of graphene exceeds 0.035 wt%, the flux shows a decreasing trend, although there is a temporary increase between 0.14~0.28 wt%.

The selectivity of a membrane is mainly influenced by the relative transport of butanol and water molecules through the membrane. Figure 5-12 presents the partial fluxes of butanol and water individually. It clearly demonstrates the relationship between selectivity and partial flux for each component. For the PIM-1/graphene MMM with graphene loading of 0.018 wt%, due to the interfacial area formation between polymer and filler, the extra free volume facilitates the transport of both butanol and water molecules, which was reflected in the flux improvement. However, possibly due to the size of interface being larger than that of channels through polymer, a slight sacrifice of selectivity is observed compared with pure PIM-1 membrane.
As the loading of graphene increases, the graphene nanofiller tends to agglomerate. This agglomeration not only hinders the permeate transfer, therefore decreasing the partial flux of both butanol and water, but also leads to the formation of some defects in the membrane, the defects favor the passage of water rather than butanol.\textsuperscript{45} It can be seen in Figure 5-12 that the flux decrease of butanol is more obvious than that of water; this is mainly attributed to the size of the water molecule which is smaller than that of butanol. It is comparatively easier for water molecule transport through the defects than relatively large size butanol molecules.\textsuperscript{46} Therefore, although both the partial fluxes decrease, the rate of change for water is less than that of butanol, which is the main reason for selectivity further decreasing.

The results in this work are in good agreement with the previous literature, Yang et al.\textsuperscript{13} studied the incorporation of graphene nanofiller in PDMS membrane and assessed the pervaporation performance for thiophene/n-octane separation, it is reported that with 0.2 wt% loading of graphene, the total flux showed 66.7% improvement compared with pristine PDMS membrane, while maintaining the enrichment factor, which is mainly attributed to the generation of large interfacial area between polymer and filler, therefore, the increased fractional free volume endows
more transfer pathways to the penetrant. Najafi et al.\textsuperscript{45} studied the incorporation of graphene in PEBA membrane for the pervaporation of isopropanol/water, it is reported that 1 wt% graphene loading gives a 34.3% increase in total flux increasing, while the separation factor also slightly increases due to the hydrophobic property of graphene. These works demonstrate that graphene, although a non-porous nanofiller, can improve the permeation property of a membrane.

However, it is noted that the selectivity of butanol over water is maintained without any improvement, Figure 5-13 labels the various kinds of hydrophobic nanoparticles (MOF, silica, Zeolite) incorporated in different kinds of polymer which were reported from previous literature, to demonstrate the effect of nanoparticles on membrane performance for butanol/water separation. As Figure 5-13 illustrates, the organophilic property of MOF (ZIF-7, ZIF-8, ZIF-71 and Zn(BDC)(TED)\textsubscript{0.5}) and Zeolite (ZSM-5) leads to the impressive selectivity for the membrane. In terms of silica, the surface functionalization of silica also endows particles with organophilic property. Therefore, from this point of view, compared with other kinds of hydrophobic nanoparticles mentioned above, the graphene nanosheet which is exfoliated from LPE method in this work seems to exhibit moderate butanol adsorption.

![Figure 5-13 The comparison of total flux and separation factor for neat polymer membranes and various nanoparticle-incorporated polymer membranes reported in](image-url)
In order to optimize the selectivity of membranes, other kinds of graphene-based fillers were studied to favor the separation process of butanol molecules over water molecules. In terms of the graphene nanosheet which is exfoliated from LPE method in this work, the majority of sheets exist in the form of few layer graphene, as confirmed by Raman spectra, and further randomly restacked in PIM-1/graphene MMMs, which may affect membrane performance.

Therefore, another exploration was conducted to apply a graphene-derivative, graphene oxide (GO). The existence of functional groups due to oxidation make it possible to functionalize various surfactants on graphene flakes. Functionalization may improve compatibility with the polymer and reduce restacking of the graphene flakes.

Our collaborator Monica Alberto et al.\textsuperscript{54} studied reduced graphene oxide (rGO) functionalised with alkyl chains. Two kinds of alkylamines with chains of different length, octylamine (OA) and octadecylamine (ODA) (8 and 18 carbon, respectively), were used to functionalize GO by reacting with carboxylic groups on the edge of the GO. The products were subsequently reduced to rGO, then mixed with PIM-1 polymer to fabricate MMMs (Figure 5-14). It is reported that the incorporation of (0.1wt% loading) rGO-OA and rGO-ODA favors the separation factor for butanol, which increased from 13.5 for a pristine PIM-1 membrane to 32.9 and 26.9 for the short chain (OA) and long chain (ODA), respectively.
This is possibly attributed to the long chain surfactant grafted on the edge of rGO improving compatibility between PIM-1 polymer and graphene flake, the surfactant effectively prevents restacking of graphene flakes and makes the graphene flakes homogenously disperse in the polymer matrix. Additionally, the rGO flake which is prepared via the Hummer method tends to generate monolayer graphene flake. AFM results confirm the existence of monolayer rGO-OA and rGO-ODA. Since rGO-OA and rGO-ODA hinder the permeation of both butanol and water molecules, acting as a “barricade” on the pathway of molecular diffusion to increase the tortuosity of the membrane, so transfer is around the rGO flakes rather than straight through the membrane, therefore the length of the diffusion pathway in the membrane is extended. Compared with the molecular transfer through MMMs with the restacked few layer graphene exfoliated via LPE method (Figure 5-15a), the transfer of butanol and water molecules in MMMs with rGO-OA and rGO-ODA (with the existence of monolayer) which homogenously disperse in the polymer matrix tend to have longer diffusion pathways, (since every homogenously dispersed graphene flake acts as a barrier to molecules) thus enhancing the separation process of butanol and water molecules (Figure 5-15b). Therefore, better butanol/water separation performance is obtained compared with graphene flake without any functionalization. This research confirms it is feasible to apply graphene based materials as nanofiller to
improve pervaporation membrane performance, in which the excellent compatibility between polymer and graphene flake, as well as homogenously dispersion of graphene in polymer matrix, are the key points to prepare high-performance MMMs.

Figure 5-15 The molecules diffusion pathway through MMMs (a) PIM-1 matrix with few layer graphene prepared via LPE method; (b) PIM-1 matrix with homogenously dispersed rGO-OA or rGO-ODA as nanofiller

5.3.5 The solvent uptake of PIM-1/Graphene MMMs

PIM-1/Graphene MMMs were tested for the effect on the uptake of butanol, which was reflected by solvent uptake testing as described in Chapter 3. Free-standing PIM-1 was tested as a comparison. The data are presented in Figure 5-16.

Figure 5-16 Solvent uptake of PIM-1/Graphene MMMs in butanol for 10 days testing
As Figure 5-16 illustrates, the incorporation of graphene decreases the uptake of butanol by the membrane, compared with pristine PIM-1. A small amount of graphene loading (0.0009 wt%) directly reduces the solvent uptake from 90.3% for pristine PIM-1 membrane to 68.5%. This is mainly attributed to the existence of large amount of free π -bonds of sp² atoms in graphene, therefore, strong non-covalent π - π interactions between PIM-1 and graphene restrict the effect of organic molecules which are trapped in the polymer matrix.

5.4 Conclusions

In this chapter, liquid phase exfoliation (LPE) of graphite was applied for mild and up-scalable preparation of graphene. Homogeneous PIM-1/graphene dispersions were obtained with PIM-1 polymer as stabilizer, which not only increased the yield of graphene in chloroform solvent, but also gave excellent dispersions. The attraction between PIM-1 molecules and graphene nanosheets is due to the π - π interaction, although after the membrane formation there is still some graphene restacking occurring due to the van der Waals attraction.

PIM-1/graphene MMMs with a series of graphene loadings were tested for pervaporation of butanol/water. It is found that a small amount of graphene loading (around 0.018 wt%) in MMMs enable the enhancement of flux while maintaining the selectivity, due to the extra interfacial space created. Additionally, the degree of swelling of the membrane was also decreased by the incorporation of graphene, due to the strong non-covalent π - π interaction between PIM-1 and graphene.

5.5 References

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Chapter 6  The Preparation of PIM-1/Fe$_3$O$_4$ Mixed Matrix Membranes for Localized Annealing
6.1 Introduction

In this chapter, PIM-1/Fe₃O₄ mixed matrix membranes were prepared to enable localized annealing by induction heating. For achieving good dispersion of Fe₃O₄ in PIM-1 solution, Fe₃O₄ nanoparticles were modified by oleic acid (OA). PIM-1/Fe₃O₄ membranes were treated under an alternating magnetic field generated by passing alternating current (AC) through a coil. Moreover, membranes were tested for the pervaporation of a butanol/water mixture. The characterization of Fe₃O₄ nanoparticles was carried out by several techniques, including X-ray diffraction (XRD), infrared spectroscopy (IR), transmission electron microscope (TEM) and thermal gravimetric analysis (TGA).

6.1.1 Background

For polymeric membranes, swelling by organic solvents is the main issue which restricts their application in pervaporation and nanofiltration.¹ By means of strong polymer-organic interactions, the organic solvent molecules are adsorbed on the surface of the membrane and trapped in the polymer matrix, which affects the membrane performance for long time usage.²

For PIM-1 polymeric membranes, in the pervaporation of butanol/water mixtures, butanol swells the organophilic membrane and water then mixes with the alcohol, reducing selectivity. Based on this, many studies have focused on controlling the swelling of PIM-1 membranes. Chemical cross-linking is one of the main options, in which the incorporation of a cross linking agent combined with post thermal treatment to achieve cross linking of the PIM-1 is desirable. A previous study used an azide-based cross linking agent to react with the nitrile group in PIM-1 via nitrene reaction. Du et al.³ reported that the cross linking of PIM-1 was formed at 175°C after 7.5 h, 4-azido phenyl sulfone was utilized to prepare crosslinked PIM-1 which exhibited good resistance to plasticization in the condensed gas. Khan et al.⁴ used self-synthesised polyethylene glycol biazide (PEG-biazide) as cross linking agent to
react with PIM-1 at 250°C.

Moreover, direct high-temperature thermal treatment was proved an effective approach for PIM-1 to achieve cross linking. Song et al.\(^5\) reported that the thermal oxidative crosslinking of PIM-1 is formed by heat treatment (350~400°C) in the presence of oxygen; free radical induced in-situ covalent crosslinking is suggested. The post treated membrane with covalently crosslinked network is chemically stable (it does not dissolve in chloroform and tetrahydrofuran), and also showed excellent selectivity for gas separation.

Although thermal treatment can achieve the cross linking of PIM-1 to relieve the swelling of membranes, it is not practical in industrial production, since for the guarantee of high performance, the thin film composite (TFC) membrane is widely applied.\(^6,7\) However, the polymer support is rarely able to resist high temperature and therefore tends to degrade. For example, for the frequently-used PVDF support, its service temperature is in a range from -40 ~ 150 °C, and the melting point is 172 °C, therefore, the total heat treatment of both PIM-1 active layer and PVDF support above 150 °C is not desirable. It is necessary to explore new thermal heating processes to heat the active layer only, while not affecting the performance of the support layer (localized annealing). Here we introduce a new idea for which we gain the inspiration from medical hyperthermia, it has potential to fulfill localized annealing in moderate circumstance and is worth exploring further.

### 6.1.2 Hyperthermia

Hyperthermia is considered as a promising approach for human cancer treatment. The fundamental concept of hyperthermia is the localized heating of the cancer area in the patient’s body. The high temperature can change the environment of the tumor cell, inhibiting tumor angiogenesis and the spread of cancer into blood vessels. This approach has been rapidly developed in the last two decades. Of various methods of hyperthermia, magnetic fluid hyperthermia (MFH) has become an emerging way, relying on the injection of thermoseeds into the tumor area of the
patient. The localized temperature heating can be realized under an external alternating current (AC) driven magnetic field, and causes the temperature in the tumor area to be maintained at 42~45℃ for several minutes, thus achieving the aim of tumor cell treatment.\textsuperscript{8} In this process, the surrounding normal body tissue will not absorb the energy which is generated from the alternating magnetic field, therefore the body tissue and bone are not affected.\textsuperscript{9} This mechanism is here considered for the localized annealing of TFC membranes to achieve the cross-linking of PIM-1. The incorporation of magnetic particles in the PIM-1 active layer and application of an alternating magnetic field could fulfill the thermal treatment of the active layer while the PVDF support layer without magnetic particles will not be affected. The structure of the membrane is shown in Fig. 6-1.

![Figure 6-1 The structure of PIM-1/magnetic particle MMM supported by PVDF](image)

**6.1.3 Fe\textsubscript{3}O\textsubscript{4} magnetic particles**

Fe\textsubscript{3}O\textsubscript{4} magnetic particles, the most commonly used magnetic particles, have an ionic crystal structure. The magnetism is size-dependent, a study reported that Fe\textsubscript{3}O\textsubscript{4} magnetic particles with particle size below 27 nm have superparamagnetism,\textsuperscript{10} which can be used for various applications, such as tissue repair, hyperthermia and drug delivery.\textsuperscript{11,12,13} Due to the excellent magnetic property and low toxicity, Fe\textsubscript{3}O\textsubscript{4} magnetic particles have drawn significant attention in medicine and biotechnology.

For the synthesis of Fe\textsubscript{3}O\textsubscript{4} nanoparticles, two important factors need to be considered: (1) Defining the experiment conditions, which lead to the monodisperse
magnetic grains with suitable particle size to maintain the superparamagnetism of the particles; (2) The appropriate reproducible process which can be industrialized without further purification treatment, such as ultracentrifugation, magnetic filtration and size-exclusion chromatography. Currently, the most commonly applied method for Fe₃O₄ preparation is the chemical coprecipitation technique.

The preparation of Fe₃O₄ by chemical coprecipitation normally uses a mixture of ferrous and ferric salts in solution. The chemical equation for Fe₃O₄ synthesis is as follows

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe₃O₄ + 4H₂O$$

According to the thermodynamics, the complete precipitation of Fe₃O₄ in the reaction is expected in the pH between 8 and 14. The Fe³⁺/Fe²⁺ ion stoichiometric ratio should be 2:1.¹⁵

### 6.1.4 Surface modification of Fe₃O₄ magnetic particle

Since Fe₃O₄ particles of nano-scale have large surface area and high surface energy as well as strong magnetic dipole interactions, they show a strong tendency to agglomeration. In the medical application, special surface treatment is necessary for Fe₃O₄ particles, which need to be nontoxic and biocompatible with body tissues. In this work, for the preparation of PIM-1/Fe₃O₄ mixed matrix membranes, it is necessary for Fe₃O₄ nanoparticles homogeneously to disperse in chloroform. Since a Fe₃O₄ nanoparticle is naturally hydrophilic due to the hydroxyl groups on the surface, therefore, a surfactant is needed to decorate the surface of the Fe₃O₄ particle in order to improve the particle stability and prevent particle agglomeration.

Oleic acid (OA) is widely applied as the surfactant to decorate the Fe₃O₄ particle, the oleic acid chemical formula is CH₃(CH₂)₇CH=CH(CH₂)₇COOH. Some studies¹⁶,¹⁷,¹⁸ have proved that a chemical bond is formed between the carboxylic group and Fe₃O₄ nanoparticles. Therefore, the chemical reaction between carboxyl group on OA and hydroxyl group on the surface of Fe₃O₄ endows the Fe₃O₄ particles
with hydrophobicity, and they disperse well in organic solvents. The reaction is presented in Fig. 6-2.

![Chemical Reaction](image)

**Figure 6-2** The chemical reaction of hydrophilic Fe₃O₄ nanoparticles surface modification with oleic acid at the temperature of 80°C

Fe₃O₄ using OA as surfactant is widely applied in biomedicine, many relevant studies have been reported previously. Ghosh *et al.*[^19] reported that Fe₃O₄ magnetic nanoparticles were capped with both oleic acid (OA) and polyethylene glycol (PEG) for hyperthermia, the decoration with surfactant OA forms oil soluble nanoparticles whereas the decoration with PEG forms hydrophilic nanoparticles. Zhao *et al.*[^20] reported that the cross-linked magnetic composite was prepared using OA-modified Fe₃O₄ nanoparticle combined with divinylbenzene (DVB) as the cross-linking agent.

In this work, OA-modified Fe₃O₄ was mixed with PIM-1 to form mixed matrix membranes. Magnetic treatment of PIM-1/Fe₃O₄ MMM was carried out under external alternating current (AC) driven magnetic field to explore the effect of localized annealing on the membranes.

### 6.2 Experimental

#### 6.2.1 Materials

PIM-1 powder (preparation described in Chapter 2, batch code: LGJ-1, Mₘ = \(1.3 \times 10^5\) Daltons, PDI = 2.2). Sodium hydroxide (NaOH, Fisher). Iron chloride hexahydrate (FeCl₃·6H₂O), iron chloride tetrahydrate (FeCl₂·4H₂O) and oleic acid were purchased from Sigma Aldrich.

The main solvents, which were purchased from Sigma-Aldrich, are chloroform (amylene stabilized), ethanol and 1-butanol.
6.2.2 Preparation of Fe$_3$O$_4$ nanoparticle

The Fe$_3$O$_4$ nanoparticles were prepared by a coprecipitation method. 27.05 g FeCl$_3$.6H$_2$O (0.01 mol) and 0.995 g FeCl$_2$.4H$_2$O (0.005 mol) were each dispersed in 100 ml water individually. NaOH aqueous solution (0.001 mol/ml) was also prepared.

80 ml FeCl$_3$.6H$_2$O solution and 80 ml FeCl$_2$.4H$_2$O solution were mixed in a three-neck flask with mechanical stirrer. The temperature was increased to 50℃, then NaOH solution was added dropwise until the pH was in the range 11~13. The reaction lasted for 1 h while keeping the temperature at 50℃. When the reaction was finished, the Fe$_3$O$_4$ particles were separated from solvent by a magnet, and washed with ethanol until the pH was neutral.

6.2.3 Surface modification of Fe$_3$O$_4$

The Fe$_3$O$_4$, prepared as described above, was dispersed in 100 ml water, which was put in a three-neck flask with mechanical stirring. The temperature was increased to 80 ℃, then 10.6 g oleic acid was added to the solution dropwise, then the reaction lasted for 1 h while keeping the temperature at 80℃. When the reaction was finished, it was washed with ethanol until the pH was neutral, then the OA-modified Fe$_3$O$_4$ powder was dried in vacuum for future use.

6.2.4 Characterization of Fe$_3$O$_4$ nanoparticle

X-ray Diffraction (XRD)

Powder diffraction patterns were obtained with an X-ray diffractometer (X’PERT, Philips) and the results compared with reference data. The Fe$_3$O$_4$ powder sample was pasted on a sample slide and then fixed on the sample holder. The X-ray tube was operated at 20 mA and 30 kV, the X-ray diffraction (XRD) pattern was recorded at a scanning rate of 2° /min. The scanned angle was set in the range of 10-80° (2θ).
Transmission Electron Microscope (TEM)

The morphology of Fe₃O₄ nanoparticles was examined using a Phillips CM20 200 kV instrument. 50 mg Fe₃O₄ nanoparticles were dispersed in 100 ml methanol under sonication for 20 min. Then a droplet of dispersed solution was put on a carbon coated copper grid and evaporated at room temperature. A CCD camera was equipped to record the particle image. The average particle size and size distribution was determined by ImageJ software.

Infrared Spectroscopy (IR)

The surface interaction of OA with Fe₃O₄ nanoparticle was characterized by infrared spectroscopy (IR). The IR spectra were recorded on a Bio-Rad FTS 6000 spectrometer as described in Chapter 2.

Thermal gravimetric analysis (TGA)

Thermogravimetric analysis was carried out for Fe₃O₄ nanoparticles with a heating rate of 10 °C/min up to 1000 °C in N₂ atmosphere using a Mettler Toledo Star@ Systems thermogravimetric analyzer as described in Chapter 2.

6.2.5 The induction heating of Fe₃O₄ solution

Two types of solution were prepared for the magnetic treatment. (1) 10 ml OA-modified Fe₃O₄ solutions were prepared with chloroform as solvent, with concentrations of Fe₃O₄ of 1, 2 and 4 mg/ml. (2) 10 ml OA-modified Fe₃O₄ solutions were prepared with PIM-1 (14 mg/ml) using chloroform, with concentrations of Fe₃O₄ of 1, 2 and 4 mg/ml.

The solutions were treated under the external alternating current (AC) driven magnetic field (Accel Instruments, TS250 Waveform Amplifier), the parameters applied were 375 kHz, 1067 W, and the current was set at 300 A. The treatment was
set to 10 min. A thermometer was used to monitor the temperature increase of the solution. Pure chloroform and pure PIM-1 solution were also treated as comparison. The setup of the experiment is presented in Fig. 6-3.

![Experimental setup for induction heating of Fe₃O₄ solution under the external alternating current (AC) magnetic field](image)

**Figure 6-3** The experimental setup for induction heating of Fe₃O₄ solution under the external alternating current (AC) magnetic field

### 6.2.6 The preparation and induction heating of PIM-1/Fe₃O₄ mixed matrix membranes (MMMs)

The PIM-1/Fe₃O₄ mixed matrix membranes were prepared by the solvent casting method as described in Chapter 3. 10 ml PIM-1 solution (14 mg/ml) in chloroform was prepared, with the addition of different concentrations of Fe₃O₄ nanoparticle as indicated in Table 6-1.

<table>
<thead>
<tr>
<th>Volume of chloroform</th>
<th>PIM-1 concentration</th>
<th>Fe₃O₄ concentration</th>
<th>Fe₃O₄ wt% in mixed matrix membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml</td>
<td>14 mg/ml</td>
<td>4 mg/ml</td>
<td>22.2 wt%</td>
</tr>
<tr>
<td>10 ml</td>
<td>14 mg/ml</td>
<td>2 mg/ml</td>
<td>12.5 wt%</td>
</tr>
<tr>
<td>10 ml</td>
<td>14 mg/ml</td>
<td>1 mg/ml</td>
<td>6.6 wt%</td>
</tr>
</tbody>
</table>
6.3 Results and Discussion

6.3.1 FTIR characterization of Fe₃O₄ nanoparticles

The FTIR spectra of unmodified Fe₃O₄ and OA-modified Fe₃O₄ nanoparticles are shown in Fig. 6-5.
In Figure 6-5, the upper (blue) line exhibits the spectrum for unmodified hydrophilic Fe$_3$O$_4$, where the sharp peak at 578 cm$^{-1}$ is the characteristic absorption peak of Fe$_3$O$_4$, which is attributed to the stretching vibration of Fe-O covalent bond. This indicates that Fe$_3$O$_4$ nanoparticles were successfully prepared. The small peak at 1637 cm$^{-1}$ corresponds to the stretching vibration of –OH group, since in the preparation of Fe$_3$O$_4$ nanoparticles using the coprecipitation method, there is a large amount of –OH groups on the surface of the Fe$_3$O$_4$ particles.

The lower (red) line illustrates oleic acid modified Fe$_3$O$_4$. The peaks at 2916 cm$^{-1}$, 2847 cm$^{-1}$ and 1404 cm$^{-1}$ correspond to –CH$_3$ and –CH$_2$– groups, respectively. The small peak at 1731 cm$^{-1}$ is the C=C double bond stretching vibration. The above absorption peaks are all consistent with the existence of oleic acid, which means that Fe$_3$O$_4$ nanoparticle has been chemically attached or physically adsorbed by oleic acid molecules.

6.3.2 XRD characterization of Fe$_3$O$_4$ nanoparticle

The crystal structure of unmodified and OA-modified Fe$_3$O$_4$ particles was investigated based on the XRD data which are presented in Figures 6-6 and 6-7. The XRD shows diffraction peaks at around 2$\theta$= 30.32°, 36.17°, 43.14°, 57.46° and 62.67°, which correspond to (220), (311), (400), (511) and (440) crystal planes, respectively. This matches well with the peaks expected for crystalline Fe$_3$O$_4$.21
The Fe$_3$O$_4$ particle size can be determined by the Scherrer Equation,\textsuperscript{22} which is written as:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where $D$ is the mean size of ordered Fe$_3$O$_4$ crystalline domains, $K$ is a dimensionless shape factor, it has typical value of about 0.9.\textsuperscript{19} $\lambda$ is the X-Ray wavelength ($\lambda = 0.15406$ nm), $\beta$ is the line broadening at half the maximum intensity, which is measured by origin software from XRD peak, $\theta$ is the Bragg angle (in degrees).

For the unmodified Fe$_3$O$_4$,  $\theta = 18.09^\circ$, $\beta = 1.13$, $D = 7.3$ nm
For the OA-modified Fe$_3$O$_4$,  $\theta = 18.13^\circ$, $\beta = 0.91$, $D = 9.1$ nm

### 6.3.3 TEM Characterization of Fe$_3$O$_4$ nanoparticles

The image of OA-modified Fe$_3$O$_4$ particle dispersion is shown in Fig. 6-8. As the Figure shows, the OA-modified Fe$_3$O$_4$ particles were spherical and exhibit excellent dispersion, this is possibly due to the presence of oleic acid preventing the particle agglomeration.
The average Fe₃O₄ particle size and size distribution were determined by ImageJ software. The average particle size calculated from TEM is 10.2 nm, this result is slightly bigger than that from the Scherrer equation, which is 9.1 nm. This can be explained by two reasons: (1) The statistical sample from TEM only represents part of the total amount of sample, therefore we are unable to contain all the particles; (2) since the Fe₃O₄ nanoparticles with particle size around 10 nm have large surface energy, which makes the internal pressure occur, therefore leading to lattice distortion, this can also affect the result from the Scherrer equation.

The particle size distribution is presented in Fig. 6-9. It is clear that around 70% by number of Fe₃O₄ particles are in a size range of 7~11 nm. Particles with large
size (15~19 nm) are also observed, with a number percentage around 12.8%. This is possibly due to Fe₃O₄ particle agglomeration, nanoparticles with large surface energy tend to form secondary particles,²² which may affect the analysis of ImageJ software and enlarge the mean particle size.

6.3.4 TGA Characterization of Fe₃O₄ nanoparticle

The TGA results of unmodified and OA-modified Fe₃O₄ are shown in Fig. 6-10.

![TGA curve](image)

Figure 6-10 TGA curves of unmodified Fe₃O₄ (blue) and OA-modified Fe₃O₄ (red)

As Fig. 6-10 illustrates, the weight loss of unmodified Fe₃O₄ (blue line) is moderate and slow, around 5 wt% total mass is lost below 300℃, which is mainly H₂O and residual ethanol from the synthesis of Fe₃O₄. For the OA-modified Fe₃O₄ (red line), the weight loss below 300℃ is attributed to the loss of H₂O and ethanol, it is clear to see a sharp decrease in the range of 300 ~ 400 ℃, this is probably due to oleic acid physically adsorbed on the Fe₃O₄ surface. The oleic acid molecule adsorbs on Fe₃O₄ particles in two forms: (1) Physical adsorption by van der Waals force; (2) chemical adsorption by covalent bond formation. Since the boiling point of oleic acid is between 350~360℃, therefore the weight loss in the range 320~400℃ is mainly due to gasification of OA molecules physically adsorbed. As temperature increases in the range of 680-750℃, another weight loss is observed. This is attributed to chemical
bonding between OA molecules and Fe₃O₄ particles, this illustrates that the existence of chemical bonding stabilizes the OA molecule more, compared with physically adsorbed. From the TGA curve, it can be determined that the OA molecule physically adsorbed on Fe₃O₄ particles is around 7.2 wt%, while the OA molecule chemically bonding to Fe₃O₄ particles is around 8.5 wt%.

6.3.5 The solvent phase transition

Since Fe₃O₄ nanoparticles are naturally hydrophilic, when added to an immiscible organic solvent/water mixture, it will disperse in the water layer. For OA-modified Fe₃O₄, since the hydrophilic COOH-side in CH₃(CH₂)₇CH=CH(CH₂)₇COOH is adsorbed on the surface of the particles, therefore the hydrophobic hydrocarbon side is exposed in the organic solvent, and so it disperses well in the organic solvent. Fig.6-11 shows the different solubility of Fe₃O₄ nanoparticles before and after modification.

As Fig. 6-11 shows, layers of water and chloroform can be seen in the tubes. When unmodified Fe₃O₄ particle are put into the mixture (left tube), it is clear that it only disperses into the water layer and is not compatible with chloroform at all. However, since the oleic acid modified Fe₃O₄ has good compatibility with organic solvent, it disperses well in chloroform instead of the water layer (right tube), which
illustrates OA-modified Fe₃O₄ disperses well in organic solvent, which provides a good foundation for the mixture of PIM-1 with Fe₃O₄.

### 6.3.6 Induction heating of Fe₃O₄ solution

Fe₃O₄ solutions in chloroform were treated in the alternating current (AC) driven magnetic field with the parameters of 375 kHz, 1067 W, and 300 A for 10 min. The temperature increases for different samples are shown in Fig. 6-12.

![Temperature increase of Fe₃O₄ solutions](image)

Figure 6-12 Temperature increase of Fe₃O₄ solutions with the Fe₃O₄ nanoparticle concentrations of 0, 1, 2 and 4 mg/ml under AC magnetic field

According to the data in Fig. 6-12, it is clear that the treatment of magnetic Fe₃O₄ nanoparticles in the alternating magnetic field increases the temperature of the solution, validating the concept of this work. The rate of change of solution temperature also increases as the concentration of Fe₃O₄ nanoparticles increases, which provides a good foundation for the thermal treatment of membranes. It should be noted that for the sample solution with 4 mg/ml Fe₃O₄ the temperature was only recorded until the 7th min, which gave a temperature of 60°C. This is because the boiling point of chloroform is 61.3°C; when the temperature is close to the boiling point, the solvent starts to splash and the experiment has to be stopped.

Moreover, after the confirmation of temperature increase with addition of Fe₃O₄ in the magnetic field, in the next stage, 10 ml mixtures with 14 mg/ml PIM-1
and Fe₃O₄ of 1, 2, 4 mg/ml were prepared to check the performance in the same magnetic field.

![Graph showing temperature increase over time](image)

**Figure 6-13** Temperature increase of PIM-1/Fe₃O₄ mixtures with Fe₃O₄ concentration of 0, 1, 2 and 4 mg/ml and PIM-1 concentration of 14 mg/ml under AC magnetic treatment

As can be seen in Fig.6-13, when PIM-1 polymer is added to Fe₃O₄ solution, the same phenomenon is observed; the temperature of PIM-1/Fe₃O₄ solution increases accordingly. The rate of temperature increase is faster with the higher concentration of Fe₃O₄ loading.

Based on the data in Figures 6-12 and 6-13, the average rates of temperature increase of each sample were calculated and are given in Table 6-2. Besides the observation of higher concentration of Fe₃O₄ leading to faster rate of temperature increase, it can also be seen that with the Fe₃O₄ concentration of 4 mg/ml, the rate of increase in pure chloroform (5.3°C/min) is higher than that in PIM-1 solution (3.8°C/min), this is possibly due to the energy generated by Fe₃O₄ nanoparticles not only heating the solvent, but also heating the PIM-1 polymer itself. With Fe₃O₄ concentrations of 1 and 2 mg/ml, the rates of temperature increase are almost the same between chloroform and PIM-1 solution, which implies little effect of polymer.
Table 6-2 Temperature increase rate of Fe₃O₄ solution and PIM-1/Fe₃O₄ mixtures with Fe₃O₄ concentrations of 0, 1, 2 and 4 mg/ml by induction heating

<table>
<thead>
<tr>
<th>Fe₃O₄ concentration</th>
<th>In chloroform</th>
<th>In PIM-1 solution (14 mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 mg/ml</td>
<td>5.3 °C/min</td>
<td>3.8 °C/min</td>
</tr>
<tr>
<td>2 mg/ml</td>
<td>2.7 °C/min</td>
<td>2.6 °C/min</td>
</tr>
<tr>
<td>1 mg/ml</td>
<td>1.9 °C/min</td>
<td>1.9 °C/min</td>
</tr>
<tr>
<td>0 mg/ml</td>
<td>0.9 °C/min</td>
<td>1.0 °C/min</td>
</tr>
</tbody>
</table>

In summary, the incorporation of magnetic Fe₃O₄ nanoparticles under the treatment of alternating magnetic field will heat the sample as expected, therefore transferring the heat to the surrounding environment. This suggests that if PIM-1/Fe₃O₄ MMMs are treated under a magnetic field, it is possible that the heat which is generated from Fe₃O₄ will be transferred to the polymer matrix, leading to the thermal treatment or even crosslinking of polymer, which could effectively prevent swelling of membranes in organic solvents.

6.3.7 The pervaporation performance of PIM-1/Fe₃O₄ MMMs

Firstly, PIM-1/Fe₃O₄ MMMs with various Fe₃O₄ loadings without magnetic treatment were applied in the pervaporation of 5% butanol and water, following the procedure as described in Chapter 2. The fresh freestanding PIM-1 membrane was also tested as comparison. The results are shown in Figure 6-14.

![Figure 6-14](image-url)
As Fig. 6-14 illustrates, the incorporation of Fe$_3$O$_4$ nanoparticles slightly depresses the separation performance of the membranes. With the increasing loading of Fe$_3$O$_4$, both flux and selectivity decrease gradually. Since Fe$_3$O$_4$ nanoparticles are non-porous fillers, homogenous dispersion in PIM-1 matrix possibly leads to partial blocking of transport pathways in the polymer and restricts the transfer of butanol and water molecules.

In terms of separation factor, since the hydrophilic Fe$_3$O$_4$ nanoparticles are functionalized by hydrophobic oleic acid molecules, good adhesion is generated between PIM-1 polymer matrix and nanoparticles, therefore no nonselective voids are formed and the separation factor is maintain around 18.8 at low loading of Fe$_3$O$_4$ nanoparticles (6.6 wt%). As the Fe$_3$O$_4$ loading increases, it is found that the separation factor gradually decreases to 16.1 at 22.2 wt% loading. This is mainly attributed to the high loading of nanoparticles tending to form agglomerates, therefore some defects might appear in the membrane, water molecules can go through these defects more easily than butanol due to the molecule size difference,$^{23,24}$ which is likely to be the main reason for separation factor deterioration.

Then, PIM-1/Fe$_3$O$_4$ MMMs with different loadings of Fe$_3$O$_4$ (6.6, 12.5 and 22.2 wt%) were treated in the magnetic field (375 kHz, 1067 W, and 300 A) to explore the effect of magnetic treatment on the performance of the membranes. The treatment times were 10 and 20 min, then the treated membranes were operated for the pervaporation. The results are shown in Figures 6-15 to 6-17. PIM-1/Fe$_3$O$_4$ MMMs without treatment are also included as a comparison.
Figure 6-15 The flux and separation factor of PIM-1/Fe$_3$O$_4$ MMMs with 6.6 wt% Fe$_3$O$_4$ loading after magnetic treatment in butanol/water pervaporation.

Figure 6-16 The flux and separation factor of PIM-1/Fe$_3$O$_4$ MMMs with 12.5 wt% Fe$_3$O$_4$ loading after magnetic treatment in butanol/water pervaporation.

Figure 6-17 The flux and separation factor of PIM-1/Fe$_3$O$_4$ MMMs with 22.2 wt% Fe$_3$O$_4$ loading after magnetic treatment in butanol/water pervaporation.
As Figs. 6-15 to 6-17 illustrate, magnetic treatment of PIM-1/Fe₃O₄ MMMs has a positive effect on the flux of membranes. Although the incorporation of Fe₃O₄ nanoparticles blocks the transport pathways in the membranes, therefore decreasing the flux, the flux is recovered to some extent by means of magnetic treatment. It is clear to see for all three membrane samples, the total flux monotonically increases with longer magnetic treatment, this is possibly attributed to the heat generated by Fe₃O₄ nanoparticles under the magnetic field affecting the thermal motion of polymer molecules, which relates to the PIM-1 structure to some extent, more free volume in the membrane is created which benefits the transfer of butanol and H₂O molecules. Moreover, the heat generation also possibly leads to the driving off of adsorbed contaminants from the membrane, therefore favoring permeation. For the selectivity, it seems that the magnetic treatment does not have an obvious effect on selectivity, for three membranes, the selectivity is still maintained in the same range after treatment.

The flux results of PIM-1/Fe₃O₄ MMMs with different Fe₃O₄ loading can be analyzed by the Maxwell model, comparing the experimental flux data with the theoretical data calculated by the Maxwell model to illustrate the effects of Fe₃O₄ nanoparticles on the PIM-1 polymer matrix and the adhesion situation of the interface between nanoparticle and matrix. The Maxwell model predicts

\[
J_{\text{MMM}} = J_p \left[ \frac{J_f + 2J_p - 2\Phi_f (J_p - J_f)}{J_f + 2J_p + \Phi_f (J_p - J_f)} \right]
\]  

(1)

where \(J_{\text{MMM}}\) is the total flux of the mixed matrix membrane, \(\Phi_f\) is the volume fraction of the dispersed nanofiller, \(J_p\) is the flux of polymer matrix and \(J_f\) is the flux of the dispersed nanofiller. The Maxwell mode is valid for systems containing spherical filler particles. The permeation through the membrane occurs in different ways which depends on the intrinsic property of nanoparticle dispersed in matrix and the interface void between particle and polymer. Therefore, several fundamentally different cases may occur.²⁷

1st case

One extreme is if there is poor adhesion between polymer and nanoparticles,
leading to the formation of non-selective voids at the interface, or if the nanoparticles themselves are very highly porous. For this extreme situation, the permeation of molecules in the nanoparticles and/or through the interfacial voids is much higher than that in the polymer matrix: \( J_f >> J_p \), the equation becomes

\[
J_{\text{MMM}} = J_p \left[ \frac{1+2\Phi_f}{1-\Phi_f} \right]
\]

If the loading of nanoparticles is low, the result can be high flux while maintaining constant selectivity. At relatively higher loading of nanoparticles, above the percolation threshold, continuous channels are formed through membrane, which tends to deteriorate the selectivity of the membrane.

2\textsuperscript{nd} case

Another extreme situation arises if the nanoparticles are non-porous, or if a porous nanoparticle is partially or completely blocked by the polymer phase. For this extreme, the permeation of molecules in the nanoparticles is much lower than that in the polymer matrix: \( J_f << J_p \), the equation becomes

\[
J_{\text{MMM}} = J_p \left[ \frac{J_p - \Phi_f J_p}{J_p + 0.5\Phi_f J_p} \right]
\]

in this case, the nanoparticle is considered as an impermeable obstacle to permeation and has no positive influence on flux.

3\textsuperscript{rd} case

Normally, the permeation of molecules transferring through the mixed matrix membranes is in the range between the two above mentioned extreme cases, \( 0 << J_f << \infty \), the nanoparticle exhibits fixed and finite permeation, which is different from that in polymer matrix. In this situation, the complete Maxwell model (Equation 1) is required to predict the flux results.

In our work, since Fe\textsubscript{3}O\textsubscript{4} nanoparticles are non-porous, the permeation through a PIM-1/Fe\textsubscript{3}O\textsubscript{4} MMM belongs to the 2\textsuperscript{nd} case. In order to obtain the
theoretical flux results calculated from Maxwell model, the weight fraction of Fe$_3$O$_4$ nanoparticle in MMMs needs to be converted to volume fraction for calculation. Since Fe$_3$O$_4$ nanoparticles in this work are modified by oleic acid, the density is not the same as that of unmodified Fe$_3$O$_3$ nanoparticles. Since $\rho_{\text{unFe}_3\text{O}_4}$ (the density of unmodified Fe$_3$O$_3$ nanoparticle) = 5.18 g/cm$^3$, $\rho_{\text{OA}}$ (the density of oleic acid) = 0.89 g/cm$^3$, according to the results in TGA analysis, in OA-modified Fe$_3$O$_3$ nanoparticle, the weight fraction of unmodified Fe$_3$O$_4$ nanoparticle is 76.5 wt%, and the weight fraction of oleic acid is 15.7 wt%, therefore, $\rho_{\text{OA-Fe}_3\text{O}_4}$ (the density of OA-modified Fe$_3$O$_3$ nanoparticle) is calculated as

$$\rho_{\text{OA-Fe}_3\text{O}_4} = \frac{m_{\text{unFe}_3\text{O}_4} + m_{\text{OA}}}{v_{\text{unFe}_3\text{O}_4} + v_{\text{OA}}} = \frac{m_{\text{unFe}_3\text{O}_4} + m_{\text{OA}}}{\rho_{\text{unFe}_3\text{O}_4} + \rho_{\text{OA}}}$$

$$= 2.85 \text{ g/cm}^3$$

Since $\rho_{\text{PIM}} = 1.056 \text{ g/cm}^3$, the volume fraction of OA-modified Fe$_3$O$_4$ nanoparticles in MMMs with a series of loadings can be determined, in which the OA-modified Fe$_3$O$_4$ loading in MMMs with 6.6, 12.5 and 22.2 wt% correspond to the volume fraction of 2.6, 5.0 and 9.6 vol% in MMMs, respectively. Therefore Equation (2) and (3) can be applied to obtain the extreme equations which correspond to 1$^{\text{st}}$ and 2$^{\text{nd}}$ case respectively.

The experimental flux results are compared with the theoretical results calculated by the Maxwell model, using Equation (3), in Figure 6-18.
Figure 6-18 The total flux performance of PIM-1/Fe₃O₄ MMMs as a function of Fe₃O₄ nanoparticle wt% in the pervaporation for 5 wt% butanol/water solution at the temperature of 65°C. The range of membrane flux according to the Maxwell model is limited by the 1st case of very highly permeable filler (red dashed line) and the 2nd case of a nonpermeable filler (blue dash line).

Figure 6-18 illustrates the experimental flux results of PIM-1/Fe₃O₄ MMMs, and the dashed lines show the limits of the range of membrane fluxes predicted by Maxwell model. Ideally, since Fe₃O₄ nanoparticles are non-porous, the experimental flux results should be on the 2nd case extreme line. However in practice, the experimental flux results are under the line and lower flux is achieved than expected. It should be noted that although 6.6 wt% loading is close to the theoretical data, as the loading of nanoparticles increases, the deviation between practical and theoretical data vary more obviously. The 2nd case already corresponds to the extreme situation that the permeation is all through the polymer matrix and no permeation is through the particle, however in our work the experimental flux is still below the theory. This may possibly be attributed to the influence of interaction between the polymer matrix and the functionalized Fe₃O₄ nanoparticles. Since the Fe₃O₄ nanoparticles were functionalized by oleic acid molecules in order to generate good adhesion with PIM-1 polymer matrix, under this circumstance the polymer rigidification may occur, in which the rigidified polymer chain layer around nanoparticle exhibits a dense structure and lower mobility in the region directly contacting the particles than the
bulk polymer matrix.\textsuperscript{28} Consequently, the free volume in the PIM-1 matrix located near the particles is reduced with the existence of interaction of oleic acid long chain on nanoparticle. It is concluded that this polymer rigidification further deteriorates the flux through the polymer matrix, leading to the experimental flux tending to be lower than the extreme case of the simple Maxwell model. It is expected that as the loading of nanoparticles increases, the rigidified polymer area tends to be larger in the MMMs, which brings greater deviation in the flux compared with the predictions of the Maxwell model.

Additionally, Figure 6-18 also demonstrate the influence of MMMs magnetic treatment on the interaction between polymer matrix and nanoparticles. It is clear to see as the magnetic treatment time increases, the experimental flux data shift from the region under the 2\textsuperscript{nd} case to the 3\textsuperscript{rd} case, even if the nanoparticle is still nonpermeable, which means the flux performance is higher than expected from the Maxwell model. This may possibly be attributed to the heat generated by Fe\textsubscript{3}O\textsubscript{4} nanoparticle under the magnetic field tending to have influence on adjacent rigidified polymer areas, which accelerate the thermal motion of polymer molecules and increase the polymer chain mobility, and thus the free volume in the polymer matrix. Therefore the reduced flux which is caused by rigidification of polymer could recover to theoretical results, and further go beyond the expected membrane flux performance.

In comparison, previous studies have also reported that the permeability of nonporous inorganic nanoparticle-filled polymeric mixed matrix membranes do not follow the permeability trend of the Maxwell model in gas separation. Ahn et al.\textsuperscript{29} report the incorporation of non-porous spherical hydrophobic fumed silica (Cabosil TS 530) in PIM-1 matrix to study the gas transfer performance variation, the results show that unlike the Maxwell model prediction of a deterioration of gas permeability, experimental data present a significant enhancement in gas permeability with the fumed silica loading in the range of 7-24 vol.\%. This is possibly attributable to the generation of new void cavities in MMMs with the addition of impermeable nanoparticles. Besides spherical nanoparticle, the addition of cylindrical and planar
nanoparticle in PIM-1 also confirm the improvement of gas transport with certain loadings. Althumayri et al.\textsuperscript{30} report that the addition of merely 0.05 vol.% few-layer graphene to PIM-1 leads to a significant increase of CO\textsubscript{2} permeability, which is possibly due to the rearrangement of polymer chains influenced by graphene nanosheet. Khan et al.\textsuperscript{31} report applying functionalized multi-walled carbon nanotubes (f-MWCNTs) mixed with PIM-1, the MWCNT have 8-12 walls and the diameter in the range 12-15 nm. It is reported that the gas permeability increased up to the loading of 1 vol.% f-MWCNTs, then decreases with further loading. These studies demonstrate that due to the interaction between polymer matrix and nanoparticle, the nonideal morphology formed in MMMs has a significant effect on membrane structure, which leads to the deviation with the expected results derived from Maxwell model in the case of MMMs ideal morphology.

### 6.3.8 The solvent uptake of PIM-1/Fe\textsubscript{3}O\textsubscript{4} MMMs

Firstly, PIM-1/Fe\textsubscript{3}O\textsubscript{4} MMMs after magnetic treatment were put into chloroform solvent to check the solubility of the membrane. It was found that the treated membranes still dissolved in chloroform, which shows that the crosslinked structure of PIM-1 polymer in MMMs is not achieved. It is possible that the heat generated by Fe\textsubscript{3}O\textsubscript{4} nanoparticles under the conditions employed is not enough for heating the PIM-1 matrix. According to Song et al.\textsuperscript{5} the crosslinked structure of PIM-1 is formed at temperatures of 350-400\textdegree C.

Then, PIM-1/Fe\textsubscript{3}O\textsubscript{4} MMMs were tested for the effect on the uptake of butanol, as described in Chapter 3. Free-standing PIM-1 was tested as a comparison. The data are presented in Fig. 6-19.
Figure 6.19 Solvent uptake of PIM-1/Fe$_3$O$_4$ MMMs (no magnetic treatment, 10 mins and 20 mins magnetic treatment respectively) with Fe$_3$O$_4$ loading of 6.6, 12.5 and 22.2 wt% in butanol solvent for 10 days.

As Fig. 6.19 illustrates, the incorporation of Fe$_3$O$_4$ nanoparticles reduces the butanol uptake, due to the inorganic property of Fe$_3$O$_4$ nanoparticles. The data also show that higher loadings of inorganic Fe$_3$O$_4$ leads to lower butanol uptake by the membranes. For the membrane with different loadings under magnetic treatment, the butanol uptake is similar compared with before treatment; this indicates the magnetic treatment does not affect the sorption properties of the membranes in butanol, regardless of the concentration of Fe$_3$O$_4$ nanoparticles.

**6.4 Conclusions**

In this chapter, PIM-1/Fe$_3$O$_4$ MMMs were prepared for the localized annealing of membranes by induction heating. Fe$_3$O$_4$ nanoparticles were successfully prepared by a chemical coprecipitation method. In order to endow good compatibility with chloroform solvent, the naturally hydrophilic Fe$_3$O$_4$ nanoparticles were modified by oleic acid (OA). The OA-modified Fe$_3$O$_4$ nanoparticles dispersed well in PIM-1 solution. Magnetic treatment of PIM-1/Fe$_3$O$_4$ dispersions confirms that Fe$_3$O$_4$ nanoparticles generate heat under external AC driven magnetic field.
Moreover, PIM-1/Fe₃O₄ MMMs with different loadings of Fe₃O₄ were prepared. Pervaporation results show that the incorporation of nonporous Fe₃O₄ nanoparticles slightly restricts the membrane performance in both flux and selectivity. The Maxwell model is applied for the prediction of total flux, the experimental flux data is slightly lower than the theoretical data, which is mainly attributed to the influence of interaction between the polymer matrix and the functionalized Fe₃O₄ nanoparticles. The polymer rigidification around the particles tends to deteriorate the flux through the polymer matrix. It is also observed that the magnetic treatment of PIM-1/Fe₃O₄ MMMs leads to the recovery of total flux, which is possibly attributed to the heat generated by Fe₃O₄ nanoparticle under the magnetic field accelerating the thermal motion of polymer molecules, thus increasing the polymer chain mobility. Therefore, the induction heating in magnetic field acts as an innovative method to adjust the morphology in MMMs and deserves the further study.

6.5 References


Chapter 7  PIM-1/Organosilicon Network Mixed Matrix Membranes for Pervaporation
7.1 Introduction

In this chapter, phenyltrimethoxysilane (PhTMS) is applied as an inorganic nanofiller to blend with PIM-1 and fabricate PIM-1/PhTMS mixed matrix membranes. Additionally, nanoparticles with inorganic network structures are also prepared using PhTMS as precursor. The inorganic network with Si-O-Si covalent bond is generated via a hydrolysis and condensation process. Nanoparticles were incorporated with PIM-1 to assess the membrane performance. The characterization of MMMs was carried out by several techniques, including infrared spectroscopy (IR), scanning electron microscopy (SEM), transmission electron microscope (TEM), thermal gravimetric analysis (TGA) and the testing of organic solvent uptake.

7.1.1 Background

Polymer membranes have advantages such as low cost of materials and ease of scale up, and therefore receive great attention in various applications, such as pervaporation and organic solvent nanofiltration. However, the inevitable problem they meet is the severe swelling in organic solvents, which will vary the polymer membrane structure over time and affect membrane behavior.

Ceramic membranes normally exhibit stable mechanical strength, excellent tolerance at extreme conditions and are more resistant to organic solvents, however, they have the drawbacks of brittleness and difficulty in scaling up. Therefore, considering the respective advantages of polymers and ceramics, polymer/ceramic mixed matrix membranes are considered as an ideal option, in which the polymer acts as the membrane matrix to guarantee the formation of a uniform membrane, and the ceramic particle acts as a nanofiller in the membrane to endow resistance to organic solvents for MMMs and restrict the swelling effect.

The interaction between polymer and inorganic nanofiller can be achieved via covalent bonds, van der Waals forces or hydrogen bonds. Mixed matrix membranes can be prepared by physical methods, dispersing the inorganic nanofillers
in the polymer dope solution, or chemical methods, post-treatment of MMM, to make the functional group on the polymer attach to the inorganic materials by covalent bonds.

Regarding the physical blending of polymer and inorganic nanofillers, many studies have reported the incorporation of a series of nanofillers in a polymer matrix to improve the membrane performance. Nanofillers include titanium dioxide (TiO$_2$), silica, zeolite, and carbon nanotubes. It is found that the incorporation of nanoparticles in the membrane strongly improves membrane performance, such as selectivity, anti-fouling ability or organic solvent resistance.

Some studies are also relevant to PIM-1/inorganic mixed matrix membranes to enhance membrane performance. Mason et al. report silicalite-1 crystals (350 nm) blended with PIM-1 polymer in pervaporation for ethanol recovery, in which silicalite-1 nanofiller was functionalized by 2-phenylethyl groups to improve hydrophobicity, thus ethanol/water selectivity of the MMMs was enhanced significantly. Zhang et al. explored the application of polyhedral oligomeric silsesquioxane (POSS) as nanoparticles within PIM-1 to fabricate electrospun fibrous membranes, the result showed that POSS particles could disperse homogenously in the polymer matrix. 40 wt% POSS in MMMs form hierarchical structures and exhibit super-hydrophobic property, which is considered as a potential candidate for industrial oil-contaminated water treatment.

### 7.1.2 Organosilicon network

Besides hydrophobic inorganic nanoparticles, introducing inorganic network fillers with polymer matrix is also studied to improve membrane performance. Among different kinds of inorganic network, organosilicon networks with siloxane linkages (Si-O-Si) are extensively studied and frequently employed. The formation of Si-O-Si is normally achieved using a two steps sol-gel process, in which an organosilicon precursor is applied to generate an organosilicon network by the process of hydrolysis and condensation. The general chemical reaction is presented below:
\[ R_x Si(OR')(4-x) + H_2O \rightarrow R_x Si(OH)(4-x) \rightarrow R_x SiO(4-x)/2 \]

in which \( R_x \) is normally methyl, phenyl or alkyl group, \( R' \) is normally a small molecular alkyl group (\( C_1 \)~\( C_6 \) aliphatic chain or aromatic chains).

The formation of Si-O-Si by a two-step sol-gel process originated from the preparation of silica aerogel. Aerogel is a type of synthetic porous material. Tetraethoxysilane (TEOS) is the commonly used precursor to produce silica aerogel via hydrolysis and condensation,\(^{12}\) the chemical reaction is presented below:

Hydrolysis:  \[ Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \]

Condensation:
- water condensation
  \[ nSi(OH)_4 \rightarrow nSiO_2 + 2nH_2O \]
- or alcohol condensation
  \[ Si(OH)_4 + Si(OC_2H_5)_4 \rightarrow 2SiO_2 + 4C_2H_5OH \]

Due to the presence of a large amount of Si-OH on the surface of silica clusters, the aerogel was endowed with hydrophilicity which is sensitive to moisture and tends to deteriorate with time.\(^{13}\) The commonly applied solution is to replace H from the Si-OH group by hydrolytically stable Si-R groups to prevent the adsorption of water.\(^{14}\)

Hedge et al.\(^{12}\) report that using hexadecyltrimethoxysilane (HDTMS) as a precursor to decorate hydrophilic silica aerogel by a sol-gel process, by means of the hydrolysis and condensation of methoxyl group on HDTMS, hydrophilic Si-OH on the aerogel surface was successfully replaced by hydrophobic Si-O-SiC\(_{16}\)H\(_{33}\), which endowed the aerogel with excellent hydrophobicity. The chemical reaction is presented below:

Hydrolysis  \[ C_{16}H_{33}Si(OCH_3)_3 + 3H_2O \rightarrow C_{16}H_{33}Si(OH)_3 + 3CH_3OH \]
Condensation

\[
\begin{array}{c}
\text{O} & \text{Si} & \text{OH} \\
- & - & - \\
\text{O} & \text{Si} & \text{OH}
\end{array}
+ C_{16}H_{33}\text{Si(OH)}_3 \rightarrow
\begin{array}{c}
\text{O} & \text{Si} & \text{O} & \text{Si} & \text{SiC}_{16}H_{33} \\
- & - & - & -
\end{array} + 3\text{H}_2\text{O}
\]

The sol-gel process is normally catalyzed by an acid or acid-base system, in which the precursor is hydrolyzed with a partial amount of water under acid conditions, then the condensation process is carried out in the presence of acid or base catalyst, such as hydrochloric acid (HCl) or ammonium hydroxide (NH\(_4\)OH). Bhagat \textit{et al.}\textsuperscript{15} report the preparation of TEOS based silica aerogels by an acid-catalyzed sol-gel process, in which TEOS was diluted in methanol and was hydrolyzed by oxalic acid, then the hydrolyzed group (Si-OH) was condensed to prepare silica aerogel. This process provides excellent control over the rates of hydrolysis and condensation by adjusting the amount of acid catalyst, and therefore has been extensively employed in sol-gel processes.

Based on this idea, some studies have investigated the incorporation of organosilicon networks with siloxane linkages (Si-O-Si) in polymer membranes. By means of post treatment of polymer/inorganic mixed matrix membranes, the functional group on the organosilicon compound can combine with the polymer by covalent bonds, van der Waals forces, hydrogen bonds or π - π interactions. Additionally, a Si-O-Si network can also be generated via a hydrolysis and condensation process between organosilicon compounds, which effectively restricts the organic solvent swelling of the membrane by creating a fully cross-linked structure.

Nunes \textit{et al.}\textsuperscript{16} reported polyetherimide (PEI)/silica MMMs with a small amount of aminopropyltrimethoxysilane (APTMS). It was observed that a well-distributed inorganic network was formed due to the interaction of amine in APTMS and the imide of PEI matrix. It was also observed that the flux was reduced with the incorporation of a network structure.

Livingston \textit{et al.}\textsuperscript{17} also investigated an organic-inorganic hybrid network in a...
membrane matrix, in which APTMS acts as the organosilicon precursor as well as crosslinking agent, blended with polyimide dope solution to fabricate PI/APTMS MMMs. With the post-treatment of 85°C heating for 19 hours, Si-OCH₃ undergoes hydrolysis and condensation to form Si-O-Si bonding, therefore generating a crosslinked inorganic network, and the amino group of APTMS reacted with the imide group of PI to generate amide group bonding. (Figure 7-1) This novel organic-inorganic network significantly prevented the membrane from swelling in organic solvents, so the flux behavior was far more stable than that of pristine PI over time.

Figure 7-1 The crosslinking chemical reaction of polyimide with APTMS via hydrolysis and condensation

Therefore, in this chapter, the research will investigate the incorporation of an organosilicon network in PIM-1 polymer in order to improve membrane pervaporation performance for butanol/water. The key point of the research is to find
a suitable organosilicon precursor which is able not only to generate an organosilicon network with siloxane linkages (Si-O-Si), but also have interaction with PIM-1 by covalent bonds, van der Waals forces, hydrogen bonds or π-π interactions, therefore inhibiting the swelling effect of organic solvent on polymer chains. It is reported by Jee that phenyltrimethoxysilane (PhTMS) (Figure 7-2), a material applied in hydrophobic polymer sieves, is capable of adsorbing butanol since it has similar solubility.\textsuperscript{18}

![Figure 7-2 The chemical structure of Phenyltrimethoxysilane (PhTMS)](image)

With regard to PhTMS, the presence of Si-O-CH\textsubscript{3} could generate an organosilicon network via hydrolysis and condensation, while the phenyl group on PhTMS can interact with PIM-1 molecular by π-π interactions. Therefore, it is expected that PhTMS is possibly an ideal candidate as a precursor to prepare PIM-1/organosilicon network mixed matrix membranes.

### 7.2 Experimental

#### 7.2.1 Materials

PIM-1 powder (prepared as described in Chapter 2, batch code: LGJ-1, M\textsubscript{w} = 1.3*10\textsuperscript{5} Daltons, PDI = 2.2). Phenyltrimethoxysilane (PhTMS, 97\%, Aldrich), Hydrochloric acid (HCl, 37\%, Fisher).

The main solvents, which were purchased from Sigma-Aldrich, are chloroform (amylene stabilized) and 1-butanol.
7.2.2 Preparation of PIM-1/PhTMS MMMs

PIM-1/PhTMS MMMs with a series of PhTMS loadings (5, 10, 20 and 30 wt%) were prepared to investigate the incorporation of PhTMS on membrane performance. Firstly, a certain amount of PhTMS liquid was added into chloroform and stirred for 3 h. Then PIM-1 powder was added to the homogenous solution and stirred for 24 h. The free-standing PIM-1/PhTMS MMMs was prepared by the solvent-casting method which is described in Chapter 3.

7.2.3 Preparation of Polyphenylsiloxane (PPhS) Network

The preparation of polyphenylsiloxane (PPhS) network was carried out via hydrolysis and condensation of PhTMS using hydrochloric acid (37%) as catalyst. 1 ml HCl was slowly added into 5 ml PhTMS liquid in a beaker dropwise, while gently shaking the beaker in order to assist the hydrolysis and condensation process. After 5 min shaking of the beaker, the total liquid in the beaker was discarded by pipette, leaving the precipitate in the beaker. Then the precipitate was washed by deionized water for 24 h to remove the residual PhTMS and HCl. The washed solid was collected by filter paper and was dried in vacuum for future use.

7.2.4 Preparation of PIM-1/ PPhS MMMs

PIM-1/PPhS MMMs with a series of PPhS loadings (5, 10, 20 and 30 wt%) were prepared to investigate the incorporation of PPhS network on membrane performance. Firstly, a certain amount of PPhS solid was added into chloroform in a sealed bottle, then 1 h sonication was carried on in order to make PPhS disperse homogenously in chloroform. Then the mixture was added to PIM-1 powder and stirred for 24 h. The free-standing PIM-1/PPhS MMMs were prepared by the solvent-casting method as described in Chapter 3.
7.2.5 Characterization

Infrared Spectroscopy (IR)

The PPhS powder, PIM-1/PhTMS membranes and PIM-1/PPhS membranes were characterized by infrared spectroscopy (IR). The IR spectra were recorded on a Bio-Rad FTS 6000 spectrometer as described in Chapter 2.

Scanning Electron Microscope (SEM)

Cross sections of free-standing PIM-1/PhTMS membranes and PIM-1/PPhS membranes were examined by a Field Emission Gun Scanning Electron Microscope (FEG-SEM Philips XL30) at an acceleration voltage of 10 keV. All the membrane sample were frozen in liquid nitrogen, fractured for cross section imaging, then coated with a Au layer (~4 nm) to prevent charging under the electron beam.

Transmission Electron Microscope (TEM)

The morphology of PhTMS and PPhS network filler was examined using a Phillips CM20 200 kV instrument. 0.1 g PhTMS and 0.1 g PPhS filler were dispersed in 50 ml chloroform respectively under sonication for 30 min. A droplet of dissolved molecules was put on a carbon coated copper grid and evaporated at room temperature. A CCD camera was used to record the particle image.

Thermal gravimetric analysis (TGA)

Thermogravimetric analysis was carried out for PhTMS and PPhS network structure filler with a heating rate of 10°C/min up to 1000°C in N₂ atmosphere using a Mettler Toledo Star@ Systems thermogravimetric analyzer as described in Chapter 2.
Determination of solvent uptake (SU)

Free-standing PIM-1/PhTMS MMMs and PIM-1/PPhS MMMs were tested for the solvent uptake (SU) by butanol for 10 days as described in Chapter 3. Free-standing PIM-1 was tested as a comparison.

7.3 Results and Discussion

7.3.1 The formation of PPhS network filler

The formation of PPhS network filler was carried out by hydrolysis and condensation using HCl as catalyst. When the HCl was added drop by drop to the PhTMS liquid (Figure 7-3a), it was observed that a white precipitate formed in the liquid along with the HCl droplet in contact with PhTMS (Figure 7-3b). After 5 min gentle stirring of the beaker for full reaction, the white solid precipitate deposited on the bottom of the beaker (Figure 7-3 c and d). The chemical reaction is presented in Figure 7-4.

![Figure 7-3](image)

Figure 7-3 The formation of PPhS network filler via hydrolysis and condensation (a) before addition of HCl, (b) 30 seconds after addition of HCl, (c) and (d) 5 min after addition of HCl.
7.3.2 FTIR characterization

The FTIR spectra of a PIM-1/PhTMS mixed matrix membrane is shown in Figure 7-5. Fresh PIM-1 membrane is also shown as a comparison.

In Figure 7-5, the lower (blue) line illustrates the spectrum for a PIM-1/PhTMS MMM, compared with the upper (red) line of a PIM-1 membrane. It is observed that three extra peaks appear in the PIM-1/PhTMS spectrum, which are indicated by dashed orange boxes, where the sharp peak at 1078 cm\(^{-1}\) is the characteristic absorption peak of Si-O-C bonding. The peak at 809 cm\(^{-1}\) is attributed to Si-C covalent bond, and the small peak at 701 cm\(^{-1}\) corresponds to the –CH\(_3\)
rocking vibration in Si-OCH$_3$. The existence of these three peaks confirms that the PhTMS has been successfully blended within the PIM-1 membrane.

Figure 7-6 illustrates the spectra of PPhS filler and a PIM-1/PPhS mixed matrix membrane. In the FTIR spectrum of PPhS filler (blue line), the strong and broad absorption band in the range of 1000~1100 cm$^{-1}$ is the characteristic absorption peak of Si-O-Si asymmetric stretching. It is observed that the broad band is separated into two small peak, which are 1026 and 1063 cm$^{-1}$, respectively, which strongly support the existence of long chain Si-O-Si covalent bonds. The sharp peak at 805 cm$^{-1}$ corresponds to the symmetric stretching vibration band of Si-O bond, and the small peak at 916 cm$^{-1}$ is attribute to the bending vibration absorption peak of Si-OH, which indicates not all the hydroxyl group are condensed to Si-O-Si bonds and still a certain amount of Si-OH remains.

In the FTIR spectra of PIM-1/PPhS MMMs (red line), it is observed that the broad absorption band in the range of 1000~1100 cm$^{-1}$ still exists, which indicates the Si-O-Si chain combines well with PIM-1 polymer, although the wavenumber of two peaks slightly change to 1056 and 1106 cm$^{-1}$.

![Figure 7-6 The FTIR spectra of PPhS filler and PIM-1/PPhS MMMs (20 wt% PPhS loading)](image)

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7.3.3 Morphology of nanofillers and mixed matrix membranes

The morphologies of PhTMS and PPhS network, deposited from chloroform, were determined by TEM. The PhTMS is presented in Figure 7-7 (a) and (b). Although PhTMS can disperse well in chloroform, some agglomeration is found in TEM image, presumably during evaporation of the chloroform solvent.

Figure 7-7 TEM images of PhTMS nanoparticle (a, b) and PPhS network (c, d)

TEM images of PPhS network are presented in Figure 7-7 (c) and (d). Unlike PhTMS, the PPhS network filler presents a totally different morphology, which appears as winding and linear chains. This is mainly attributed to the occurrence of hydrolysis and condensation process, which possibly influences the macroscopic
morphology of PPhS.

The cross section morphologies of PIM-1/PhTMS and PIM-1/PPhS MMMs were studied by SEM. PIM-1/PhTMS MMMs with 10 wt% and 30 wt% PhTMS loading are presented in Figure 7-8 (a) and (b), respectively. It is clear to see that 10 wt% PhTMS disperses homogenously within the PIM-1 matrix and no agglomeration is found. As the loading of PhTMS in MMMs increases to 30 wt%, it is observed that PhTMS varies the morphology of the membrane matrix tremendously compared with that of 10 wt% loading, in spite of this, it is found that PhTMS is still homogenously distributed, which confirms the excellent combination between PhTMS molecules and PIM-1 polymer.

Figure 7-8 Cross sectional SEM image of PIM-1/PhTMS and PIM-1/PPhS MMMs (a) PIM-1/PhTMS MMMs with 10 wt% PhTMS loading (b) PIM-1/PhTMS MMMs with 30 wt% PhTMS loading (c) PIM-1/PPhS MMMs with 10 wt% PPhS loading (d) PIM-1/PPhS MMMs with 30 wt% PPhS loading.

PIM-1/PPhS MMMs with 10 wt% and 30 wt% PPhS loading are presented in Figure 7-8 (c) and (d), respectively. Compared with the smooth morphology of pristine
PIM-1 membrane, the incorporation of PPhS filler in the polymer matrix strongly affects the morphology of the membrane. The cross sections exhibit more roughness as the loading of PPhS increases. It is noteworthy to see the grainy particle distribution in the polymer matrix in 30 wt% PIM-1/PPhS membrane, this is possibly due to the high loading of PPhS filler leading to the nanoparticle agglomeration.

7.3.4 TGA Characterization of PPhS Filler

The TGA result for PPhS filler is shown in Figure 7-9.

![TGA Curves of PPhS Filler](image)

Figure 7-9 TGA curves of PPhS filler

As Figure 7-9 illustrates, two main degradation steps exist in the TGA curve. The first weight loss, which is around 5%, is in the range of 250 ~ 370 °C, this is probably due to the chain scission of Si-OH, the presence of which has been confirmed via FTIR in Section 7.3.2. The second stage weight loss, which is in range of 470 ~ 620 °C, represents a large decrease, around 17%, this is mainly attributed to the chain scission of Si-O-Si bonds. This high degradation temperature is probably due to the high bond energy of Si-O, 451 kJ/mol, which endows excellent thermal and chemical stability to PPhS filler.

7.3.5 Solvent uptake testing

PIM-1/PhTMS and PIM-1/PPhS MMMs were assessed for the effect on the
membrane swelling of butanol, which was partially reflected by solvent uptake testing as described in Chapter 3. Free-standing PIM-1 was tested as a comparison. The data are presented in Figure 7-10.

![Graph showing solvent uptake of PIM-1/PhTMS and PIM-1/PPhS MMMs](image)

Figure 7-10 Solvent uptake of PIM-1/PhTMS and PIM-1/PPhS MMMs (with nanofiller loading of 0, 5, 10, 20 and 30 wt%, from left to right) in butanol for 10 days. Solvent uptake in Y-axis starts from 25 as baseline.

From Figure 7-10, it is observed that the incorporation of PhTMS and PPhS filler significantly reduces the organic solvent uptake of the membrane compared with pristine PIM-1. For both fillers, a small amount of loading (5 wt%) directly reduces the solvent uptake from 90.3% for pristine PIM-1 membrane to around 50%. Higher loadings further reduce the solvent uptake of the membrane, down to around 30% when the filler loading increases to 30 wt%. This is possibly attributed to the existence of a large amount of phenyl groups in both PhTMS and PPhS, non-covalent π - π interactions between PIM-1 and filler restrict the effect of organic molecules which are trapped in the polymer matrix.

### 7.3.6 Pervaporation performance of MMMs

PIM-1/PhTMS MMMs with PhTMS loadings of 5, 10, 20 and 30 wt% and PIM-1/PPhS MMMs with PPhS loadings of 5, 10, 20 and 30 wt% were tested in the pervaporation of 5% butanol and water, following the procedure described in Chapter
3. The fresh freestanding PIM-1 membrane was also tested as comparison. The flux performance of the membranes is shown in Figure 7-11.

![Figure 7-11](image)

Figure 7-11 The total flux performance of PIM-1/PhTMS MMMs and PIM-1/PPhS MMMs with 5, 10, 20 and 30 wt% nanofiller loadings, in pervaporation of butanol/water with 5 wt% feed solution at the temperature of 65°C, Flux in Y-axis start from 1.0 as baseline.

Figure 7-11 illustrates the effect of PhTMS and PPhS filler on the membrane flux performance. It is observed that the flux through the mixed matrix membranes gradually decreases as the loading of filler increases, with the exception of PIM-1 with 30 wt% PhTMS. These results are consistent with the solvent uptakes exhibited in section 7.3.5. With higher loading of filler, there is less butanol solvent uptake, i.e. lower liquid-phase sorption coefficient $K_i$, and thus reduced flux according to the solution-diffusion model (see Section 1.5.3).

Both PhTMS and PPhS lead to a deterioration in total flux, but the mechanisms are different. PhTMS acts as a molecular species, its suitable molecular size scale allows PhTMS to fill the micropores of PIM-1 at low loadings, this occupation directly reduces the free volume of the membrane and thus the total flux, while at higher loading of PhTMS (around 30 wt% loading), phase separation between PIM-1 matrix and PhTMS may occur, in which case microvoids formed at the boundary enhances the flux.

In terms of PPhS particles, since its particle size scale is larger than the pore
size of PIM-1 polymer, therefore the free volume of PIM-1 polymer is rarely occupied by PPhS. The decrease of flux is possibly attributed to the non-porous PPhS particles hindering the transfer of permeate. It is noteworthy that when comparing the PIM-1/PhTMS MMMs and PIM-1/PPhS MMMs with the loadings of 5, 10, 20 wt%, the flux of PIM-1/PhTMS MMMs is higher than that of PIM-1/PPhS MMMs with same filler loading. This indicates that the influence of non-porous PPhS particles on total flux is more obvious than that of PhTMS molecules. The loading of 30 wt% PPhS is still distributed well in the polymer matrix, with the existence of phenyl groups on the particle surface, and no phase separation is observed in the membrane cross sectional SEM image presented in Figure 7-8(d).

These flux results for the incorporation of organosilicon filler in our experiments are consistent with results reported by Livingston et al.\textsuperscript{17} for the addition of APTMS in a polyimide membrane. It seems that the incorporation of organosilane filler or its derivative organosilicon network does not favor the diffusion process of penetrant through the membrane.

Figure 7-12 illustrates the effects of PhTMS and PPhS filler on the membrane separation factor performance.

![Figure 7-12](image)

Figure 7-12 The separation factor of PIM-1/PhTMS MMMs and PIM-1/PPhS MMMs with 5, 10, 20 and 30 wt% nanofiller loading in pervaporation of butanol/water with 5 wt% feed solution at the temperature of 65°C, separation factor in Y-axis start from 12 as baseline.
With regard to PIM-1/PhTMS MMMs, it is observed that the separation factor gradually decreases from 20.2 in fresh PIM-1 to 16.4 in PIM-1/PhTMS with 20 wt% filler. The deterioration of separation factor with the addition of PhTMS in PIM-1 is opposite to the expected, it is reported by Jee et al.\textsuperscript{18} that PhTMS has similar solubility to butanol. For PhTMS, its relative affinity to butanol and water molecules can be determined by Hansen’s solubility parameter (δ), which is affected simultaneously by three types of interaction: δ\(_h\) (the hydrogen bonding interaction), δ\(_p\) (the polarity interaction) and δ\(_d\) (the dispersion interaction), the interaction of two components is determined by the distance parameter Δ, which is calculated by Equation

\[
\Delta_{A-B} = \sqrt{(\delta_{d,A} - \delta_{d,B})^2 + (\delta_{p,A} - \delta_{p,B})^2 + (\delta_{h,A} - \delta_{h,B})^2}
\]

The solubility parameters for PhTMS, butanol and water are presented in Table 7-1

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ(_d) (MPa(^{1/2}))</th>
<th>δ(_p) (MPa(^{1/2}))</th>
<th>δ(_h) (MPa(^{1/2}))</th>
<th>δ (MPa(^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhTMS</td>
<td>19.7</td>
<td>3.3</td>
<td>4.4</td>
<td>20.4</td>
</tr>
<tr>
<td>butanol</td>
<td>16.0</td>
<td>5.7</td>
<td>15.8</td>
<td>23.2</td>
</tr>
<tr>
<td>water</td>
<td>15.6</td>
<td>16.0</td>
<td>42.3</td>
<td>47.8</td>
</tr>
</tbody>
</table>

Therefore, the calculated distance parameter Δ\(_{\text{PhTMS-butanol}}\) is 12.2 MPa\(^{1/2}\) while the distance parameter Δ\(_{\text{PhTMS-water}}\) is 40.2 MPa\(^{1/2}\), which indicates PhTMS molecules interact with butanol more strongly than with water in theory.

However, in our experimental results, the incorporation of PhTMS in PIM-1 does not exhibit an improvement of separation factor. This could be analyzed in terms of two factors: In terms of the adsorption process, the water contact angle of the membrane surface provides direct characterization. Araki et al.\textsuperscript{21} reports the water contact angle of PhTMS silica membrane is around 83°, which is slightly less hydrophobic than the PIM-1 membrane (contact angle is 86°). It seems that, compared with neat PIM-1 membrane, the PhTMS membrane does not exhibit the adsorption superiority towards butanol molecules as expected. In terms of the
diffusion process through the membrane, the occupation of PhTMS molecules in the pores of PIM-1 significantly decreases the polymer free volume, therefore hindering transport of butanol molecules through membrane. This effect is more obvious at loadings of PhTMS up to 20 wt%. Therefore, considering the effect of PhTMS on both adsorption and diffusion processes, this may lead to the decrease of separation factor.

It is noticeable that when the loading of PhTMS reaches 30 wt%, the separation factor recovers back to 18.7, this is possibly attributed to the higher loading of PhTMS leading to phase separation of PIM-1 matrix and agglomerated PhTMS, butanol and water molecules tend to transfer through unfilled polymer matrix which makes the separation factor recover back.

With regard to PIM-1/PPhS MMMs, the results show that the loadings of 5 wt% and 10 wt% PPhS have little effect on separation factor, which is similar to that of neat PIM-1 membrane. When the loading increases to 20 wt%, the separation factor reduces to 18.3, and further sharply decreases to 14.4 at 30 wt% loading. This is attributed to the agglomeration of high loading PPhS filler, forming defects through the membrane which favors the passage of water rather than butanol. Therefore, compared with PhTMS, the slight addition of PPhS filler (5~10 wt%) could still maintain the original selectivity of the membrane.

PhTMS is a commonly applied organosilane with phenyl group. Not only can it be used as the precursor of a hydrophobic silica membrane, prepared via hydrolysis and condensation, but it can also be applied as the coated layer on a polymer membrane, by the sol-gel condensation method, to improve the adsorption affinity to a penetrant. Compared with the applications of PhTMS reported in literature, this work is the first report of the direct incorporation of PhTMS and PhTMS-derived nanofiller (PPhS) in a polymer matrix with physical blending for the pervaporation of butanol/water. Unlike Jee et al. who reported that the coated PhTMS on PDMS membrane surface favors both total flux and selectivity in butanol/water pervaporation, the physical blending of PhTMS and PPhS filler in a PIM-1 matrix do not exhibit performance improvement in this work. Therefore, it is
concluded that PhTMS organosilane tends to favor the butanol molecule adsorption process on the membrane surface rather than the diffusion process through the membrane in pervaporation.

In addition to PhTMS, there are also other kinds of organosilane which have been studied to optimize membranes for pervaporation of butanol/water. Araki et al.\textsuperscript{21} reported the application of several kinds of organosilane, such as PhTMS, ethyltrimethoxysilane (ETMS), n-propyltrimethoxysilane (PrTMS), isobutyltrimethoxysilane (BTMS) and hexyltrimethoxysilane (HTMS) as the precursors of silica membranes, and the pervaporation for butanol/water was also tested. It was observed that, compared with PhTMS and BTMS silica membranes, the ETMS, PrTMS and HTMS silica membranes exhibit superior behaviour in both flux and separation factor, which is mainly attributed to these three types materials having closer Hansen solubility parameters with butanol than PhTMS and BTMS. Moreover, organosilane can be applied as a coupling agent to decorate the hydrophilic nanoparticle for the enhancement of hydrophobicity. The modified nanoparticles can be mixed with polymer to favor the MMMs performance. Zhou et al.\textsuperscript{25} report the application of vinyltrimethoxysilane (VTMS) to decorate silicate-1 via hydrolysis and condensation reaction, the VTMS-modified silicate-1 particle was incorporated with PDMS to fabricate hybrid membranes for pervaporation of butanol/water. It was observed that with the modification of VTMS, excellent adhesion is formed between the interface of PDMS and silicate-1 particles, which not only improves the selectivity for butanol, but also improves membrane long-term stability. Figure 7-13 shows pervaporation results for butanol/water of both silica membranes, with different kinds of organosilane as precursor, and polymer membranes which were coated by organosilane or using organosilane-modified nanoparticles, reported in previous literature, as well as PIM-1/PhTMS and PIM-1/PPhS MMMs for comparison in this work. It should be noted that the PIM-1 based membranes offer substantially higher fluxes than the other materials reported here, even allowing for some loss of flux on adding PhTMS or PPhS. Furthermore, these high fluxes are achieved with separation factors that are only exceeded by a handful of materials.
Figure 7-13 The comparison of total flux and separation factor in pervaporation of butanol/water about PIM-1/PhTMS and PIM-1/PPhS MMMs with other PhTMS-related membrane reported in literature. Symbols: (1) neat PIM-1, PIM-1/PhTMS MMMs, PIM-1/PPhS MMMs (this work); (2) PDMS/PVDF membrane, PhTMS/PDMS/PVDF membrane (Jee et al.); (3) PDMS/ceramic (20 °C), PhTMS/PDMS/ceramic (20 °C), PDMS/ceramic (30 °C), PhTMS/PDMS/ceramic (30 °C); (4) PDMS/ceramic (40 °C), PhTMS/PDMS/ceramic (40 °C) (Kim et al.); (5) unmodified silicate-1/PDMS membrane, PrTMS silica membrane, VTMS-1/PDMS membrane (Zhou et al.);

Therefore, it is necessary to discuss the organosilane family in the application of membrane separation. Much previous literature has studied the potential of various kinds of organosilane to fabricate membranes, that is, they can act as raw materials to prepare silica membranes by the sol-gel method for pervaporation. Additionally, organosilane can be also used in polymer membranes to fabricate mixed matrix membranes (MMMs) or thin film composite (TFC) membranes to favor the membrane performance by different schemes (Figure 7-14) which have been reported in the literature: (1) organosilane can be coated on the surface of a polymer membrane via sol-gel condensation to increase the hydrophobicity of the membrane surface and therefore increase the affinity to certain organic molecules; (2) organosilane can generate silica particles via self-condensation, which can be incorporated in a polymer membrane to adjust and optimize the polymer chain.
packing, therefore improving flux (or selectivity)\textsuperscript{27} (Figure 7-14 b); (3) organosilane can act as a surfactant, which is used for the surface modification of nanoparticles, to generate excellent compatibility between the polymer matrix and the nanoparticle\textsuperscript{25,28} (Figure 7-14 c) (4) organosilane can be applied as a crosslinking agent in the polymer membrane by forming a stable covalent bond with the functional group of a polymer chain to form a network structure and change the morphology of the membrane, which possibly favors the selectivity and promotes the membrane stability in long term use\textsuperscript{27,17} (Figure 7-14 d); (5) organosilane can also play the role as an intermediate layer between the active layer and support to provide good adhesion, since the swelling of a polymer membrane normally happens in organic aqueous solution separation, which lead to a loose combination between the active layer and the support, therefore deteriorating the performance. The organosilane can not only react with polymer in the active layer, but also act as an anchor to the support, which leads to the strong binding between the active layer and the support to maintain TFC membrane stability in organic aqueous solution.\textsuperscript{29} (Figure 7-14 e)

Figure 7-14 The schematic presentation of applying organosilane to optimize a TFC membrane by different methods: (a) organosilane coated on membrane surface; (b) silica nanoparticle using organosilane as precursor; (c) organosilane-modified nanoparticle mixed in polymer matrix; (d) organosilane as cross linking agent to generate network with polymer; (e) organosilane as intermediate layer between active layer and support.
Unlike the cases for organosilane application mentioned above, our work is the direct incorporation of PhTMS in a polymer matrix with physical blending, while PPhS silica nanoparticle is generated via the hydrolysis and condensation derived from PhTMS as precursor, which belong to the 2nd case. Unfortunately, the direct physical blending of PhTMS in PIM-1 matrix does not improve membrane performance as expected. Additionally, in terms of the reaction tendency of PPhS nanoparticles via the hydrolysis and condensation, this is mainly attributed to the chemical structure of PhTMS organosilane. Although organosilane family can be applied by various schemes to combine with polymer membranes, as mentioned above, the specific application of different organosilanes is determined by their molecular structure and the functional groups they possess. It is expected that the structure and properties of various organosilanes will determine their physical chemical properties, which include the hydrolysis ability, self-condensation tendency, thermal stability and reactivity with polymer matrix, therefore directly influencing the performance of MMMs. Xia et al. particularly illustrates the influence of different functional groups of organosilanes on their reaction tendency and further the scheme to incorporate with polymer membranes. In the study, three representative organosilanes were chosen to mix with PVA polymer to prepared PVA/organosilica MMMs for pervaporation of ethanol/water, which are PhTMS, dimethoxydiphenylsilane (DMDPS) and aminopropyltrimethoxysilane (APTMS), which correspond to the organosilane with one phenyl group, two phenyl groups and amino group. Generally, organosilane will firstly be hydrolyzed in water to form hydroxyl groups, while further reaction tendency (self-condensation or reaction with polymer) was determined by the chemical structure of the organosilane molecule. The experiment illustrated that hydrolyzed APTMS with –NH$_3$ have a good dispersion in PVA solution, meanwhile the crosslinked structure with PVA polymer can be easily achieved (Figure 7-15). In contrast, hydrolyzed PhTMS and DMDPS molecules tend to have further self-condensation reaction, which leads to the organosilica particle precipitate. PhTMS molecule with three hydroxyl groups react with each other to form a network structure (Figure 7-16), while DMDPS molecule with two hydroxyl
groups generate a linear structure (Figure 7-17).

![Figure 7-15](image1)

Figure 7-15 The covalent bond reaction between hydrolyzed APTMS and PVA to generate a crosslinked structure.

![Figure 7-16](image2)

Figure 7-16 The condensation reaction of hydrolyzed PhTMS to generate a network structure of silica.

![Figure 7-17](image3)

Figure 7-17 The condensation reaction of hydrolyzed DMDPS to form linear structure of silica.

This difference in reaction tendency is mainly attributed to the existence of phenyl group. For organosilane molecule without phenyl group, it is comparatively easy to react with polymer chain and has less tendency to generate silica particle via self-condensation, therefore, this type of organosilane is normally considered as the first choice of crosslinking agent for polymer matrix, such as APTMS and VTMS.

For organosilane molecule with phenyl group, it restricts the reaction with
the –OH group on PVA chains due to steric hinderance, thus making it difficult to form a crosslinked polymer structure and have more tendency to generate silica particle via self-condensation, such as DMDPS and PhTMS. It is also observed that DMDPS molecule with two phenyl groups exhibits a higher tendency of self-condensation than PhTMS molecule, due to the higher content of phenyl groups and lower content of hydroxyl groups after hydrolysis, which makes the DMDPS molecule more hydrophobic and tends to repel the water molecules and approach each other compared with PhTMS molecule.

7.4 Conclusions

In this chapter, PhTMS is employed to blend with PIM-1 and fabricate mixed matrix membranes. PPhS network with Si-O-Si covalent bond is also prepared via a hydrolysis and condensation process using PhTMS as precursor. PIM-1/PhTMS MMMs and PIM-1/PPhS MMMs were fabricated for the pervaporation of butanol/water. In theory, PhTMS has similar solubility parameter with butanol (20.4 MPa$^{1/2}$ and 23.2 MPa$^{1/2}$, respectively), the calculated distance parameter $\Delta_{\text{PhTMS-butanol}}$ is 12.2 MPa$^{1/2}$ while the distance parameter $\Delta_{\text{PhTMS-water}}$ is 40.2 MPa$^{1/2}$, which indicates PhTMS molecules interact with butanol more strongly than with water. However, experimental results show that the incorporation of PhTMS does not improve the selectivity of the membrane as expected, which is possibly attributed to the occupation of PhTMS molecules in the pores of PIM-1 significantly decreasing the MMMs free volume. Furthermore the lower butanol solvent uptake in the MMMs also reduces the flux through the membrane.

In terms of PPhS particles, due to the larger particle size scale than pore size of PIM-1, the decrease of flux is possibly attributable to the non-porous PPhS particle leading to a resistance to permeation. A slight addition of PPhS filler (5–10 wt%) could still maintain the original selectivity compared with neat PIM-1 membrane. Moreover, the reaction tendency of various organosilanes is extensively discussed, which is determined by their molecular structure and the functional groups they
possess. The organosilanes with phenyl group (such as PhTMS and DMDPS) are likely to be restricted in the reaction with polymer functional groups due to steric hinderance and tend to generate silica particles via hydrolysis and self-condensation.

### 7.5 References

Chapter 8  Conclusions and Future Work
8.1 Conclusions

In this project, the representative polymer in the polymers of intrinsic microporosity (PIMs) family, PIM-1, was extensively studied in pervaporation for alcohol recovery. PIM-1 polymer was synthesized by the high temperature method and fully characterized using various techniques, including GPC, NMR, ATR-IR, TGA and nitrogen sorption analysis.

A PIM-1 free-standing membrane was fabricated via the solvent casting method and explored for application in pervaporation of ethanol/water and butanol/water mixtures. The results show that the performance of a PIM-1 membrane (both flux and selectivity) in separation of butanol/water ($J_{\text{b}}=1.85$ kg m$^{-2}$ h$^{-1}$, $\beta_{\text{b}}=19.2$) is superior to that of ethanol/water ($J_{\text{e}}=0.62$ kg m$^{-2}$ h$^{-1}$, $\beta_{\text{e}}=2.8$), which is mainly attributed to the close chemical affinity between the PIM-1 membrane and the butanol molecule, as well as the relatively weaker interaction between butanol and water compared with ethanol and water, as determined by Hansen’s solubility parameters. Additionally, the selectivity ($\alpha$) of free-standing PIM-1 is also calculated, to demonstrate the intrinsic PIM-1 material properties for butanol/water separation. The $\alpha$ value (1.97) in pervaporation of butanol/water operated in 65°C of this work is slightly lower than that reported by Žák et al.$^1$ for a PIM-1 membrane with thickness of 42 $\mu$m used in pervaporation at 50°C ($\alpha$ value in range of 2~6), which is possibly attributable to different conditions and the experimental parameters. Comparing the free-standing PIM-1 pervaporation results of butanol/water with other pervaporation membrane candidates reported in previous literature, the PIM-1 membrane exhibits excellent flux performance while maintaining moderate selectivity. the flux performance in this work is superior to PDMS$^{2,3}$ and PEBA$^4$, just slightly lower than reported for a PTMSP membrane.$^5$ Therefore, the research focused on the optimization of PIM-1 membranes in butanol recovery via pervaporation.

In order to optimize the membrane productivity to meet the demands of industrial application, PIM-1 based thin film composite (TFC) membranes were fabricated, in which PIM-1 acts as the active layer and polyvinylidene fluoride (PVDF)
was chosen as support. Home-made PVDF supports, fabricated using a series of PVDF dope solutions (18, 20 and 22 wt%), were characterized by SEM, AFM and water contact angle. The results show that the PIM-1 active layer coated on PVDF (18 wt%) have better performance than that of 20 and 22 wt%, which is mainly attributed to the high surface porosity (52%) and the large mean pore size (54 nm) of the PVDF 18 support materials, which provide more pathways for permeation compared with PVDF 20 and PVDF 22. Additionally, the PVDF support was optimized using phosphoric acid as additive. The results show that phosphoric acid exhibits impressive pore-inducing ability and effectively controls the surface porosity and pore size distribution of the support. The incorporation of 3 wt% and 5 wt% phosphoric acid in PVDF dope solution could improve the surface porosity from 52% in neat PVDF 18 to 69% and 62%, respectively, and adjust the average pore size from 43.2 nm in neat PVDF 18 to 43 nm and 25 nm, respectively, which favor the higher flux and minimize the risk of active layer defects compared with neat PVDF 18 support.

In terms of the analysis of the PIM-1 active layer, the thickness is adjusted by adjusting the concentration of the PIM-1 dope solution in dip-coating. It is observed that the PIM-1 active layer increases from 0.98~1.24 μm for 2 wt% to 2.04~2.23 μm for 3 wt%, reaching 2.72~2.95 μm for 4 wt% PIM-1 solution, regardless of the type of PVDF support. Total flux of the TFC membrane deteriorates as the thickness of the active layer increases, which follows well with Fick’s law of diffusion. Additionally, the flux of TFC membranes is also observed to be proportional to the surface porosity of the support and the separation factor is enhanced as the surface porosity, which all indicates the significant effect of the porosity of the support on the total performance of the membrane. An impressive flux of 9.08 kg m⁻² h⁻¹ is obtained via PVDF 18-A3 coated in 2% PIM-1 solution, while maintaining the separation factor of 13.3, which is superior to the performance of a commercial PDMS membrane \( (J = 5.25 \text{ kg m}^{-2} \text{ h}^{-1}, \ \beta = 9.9) \) from Pervatech tested under the same experimental conditions, and commercial PDMS Pervap 4060 (Sulzer) \( (J = 3.4 \text{ kg m}^{-2} \text{ h}^{-1}) \) reported in previous literature.⁶

In order to further improve the membrane performance in butanol recovery,
PIM-1 based mixed matrix membranes (MMMs) were also studied. Various inorganic nanofillers (graphene, Fe$_3$O$_4$ and organosilicon network) were explored to incorporate into a PIM-1 polymer matrix with excellent compatibility. With regard to graphene, PIM-1/graphene MMMs were fabricated via liquid phase exfoliation (LPE) of graphite with PIM-1 as stabilizer to obtain homogeneous PIM-1/graphene solutions. It is observed that with the existence of PIM-1 polymer, the graphene dispersions are extremely stable and no sediment is found, even two years after the sample was prepared, which is mainly attributed to noncovalent interactions ($\pi$-$\pi$ interactions) between PIM-1 and graphene, which favor PIM-1 attaching to the basal plane of graphene to prevent the graphene from restacking and to maintain their stable dispersion in PIM-1 solution. Afterwards, PIM-1/graphene MMMs with different graphene loadings were prepared and assessed in the pervaporation of butanol/water. A small amount of graphene loading (around 0.018 wt%) in MMMs enable the enhancement of flux (2.03 kg m$^{-2}$ h$^{-1}$, 11% increase compared with neat PIM-1 membrane) while maintaining the separation factor, due to the extra interfacial space created between polymer and graphene. Compared with the graphene nanosheet which is exfoliated from LPE method in this work, Alberto et al.$^7$ report that octylamine (OA) and octadecylamine (ODA) modified rGO could favor the exfoliation of graphene (with existence of monolayer) and homogenously disperse in PIM-1 polymer matrix. Longer diffusion pathways endowed by graphene flakes in the membrane enhance the separation process of butanol and water molecules, therefore improving the separation factor from 13.5 for a pristine PIM-1 membrane to 32.9 and 26.9 for OA and ODA, respectively.

With regard to Fe$_3$O$_4$ nanoparticles, PIM-1/Fe$_3$O$_4$ MMMs were fabricated for localized annealing by induction heating. Since Fe$_3$O$_4$ nanoparticles have large surface area and high surface energy which leads to a strong tendency of agglomeration, oleic acid (OA) is applied as the surfactant to decorate the Fe$_3$O$_4$ particles, which leads to homogenous dispersion in chloroform and endows good adhesion between PIM-1 matrix and Fe$_3$O$_4$ nanoparticles. Magnetic treatment of PIM-1/Fe$_3$O$_4$ dispersions confirms Fe$_3$O$_4$ nanoparticles generate heat under external
AC driven magnetic field. However, possibly due to insufficient heat generated, the crosslinking of PIM-1 polymer was not achieved, meanwhile, results show that the incorporation of Fe$_3$O$_4$ nanoparticle slightly restricts the membrane performance in both flux and selectivity. The experimental flux result is slightly lower than the theoretical result which is predicted via the Maxwell model, which is possibly attributed to nonideal morphology structure of PIM-1/Fe$_3$O$_4$ MMMs. With the oleic acid as surfactant, good interaction is formed between PIM-1 polymer matrix and Fe$_3$O$_4$ nanoparticles, but under this circumstance polymer rigidification may occur, in which the rigidified polymer chain layer around the nanoparticles exhibits lower mobility in the region directly contacting the particles than in the bulk polymer matrix, thus leading to a deviation in the flux compared with predictions of the Maxwell model. It is noted that after the magnetic treatment, the experimental flux tends to recover back to the theoretical value, this is possibly attributed to the heat generated by Fe$_3$O$_4$ nanoparticle accelerating the thermal motion of adjacent rigidified polymer area, increasing the polymer chain mobility, and thus the free volume in the polymer matrix. Therefore, magnetic treatment using Fe$_3$O$_4$ nanoparticles is a potentially innovative idea to adjust nonideal morphology of MMMs, and deserves further study.

With regard to phenyltrimethoxysilane (PhTMS), it is applied as a precursor to prepare organosilicon network (PPhS) via hydrolysis and condensation. FTIR spectra show a strong absorption band in the range of 1000~1100 cm$^{-1}$, which confirms the existence of long chain Si-O-Si covalent bonds. Thereafter PIM-1/PhTMS and PIM-1/PPhS MMMs are fabricated with a series of PhTMS and PPhS loadings (5 wt%, 10 wt%, 20 wt% and 30 wt%). The cross section images of membranes via SEM exhibit homogenous dispersion of nanoparticles in MMMs. In the evaluation of pervaporation of a butanol/water mixture, the results show that the incorporation of PhTMS and PPhS do not improve the flux and separation factor of the membrane as expected. This is possibly attributed to PhTMS acting as molecular species, at low loadings it will most likely fill free volume of PIM-1 and so reduce flux of membrane. PPhS act as a non-porous nanoparticle, hindering the transfer of permeate. Although PhTMS has similar solubility parameter with butanol (20.4 MPa$^{1/2}$.
and 23.2 MPa, respectively), and Jee et al.\(^8\) reported that the coated PhTMS on PDMS membrane surface favors both total flux and selectivity in butanol/water pervaporation, however, the direct incorporation of PhTMS and PPhS in polymer does not favor the butanol recovery from aqueous solution.

Comparing the three types of PIM-1 based MMMs in this project (PIM-1/graphene MMMs, PIM-1/Fe\(_3\)O\(_4\) MMMs and PIM-1/Organo-silicon network MMMs), the study of each type of mixed matrix membrane has unique significance. The incorporation of nonporous filler, graphene flake, leads to a maximum 11% flux improvement compared with neat PIM-1, which confirms the addition of nonporous filler can improve the flux by generating extra free volume. In terms of Fe\(_3\)O\(_4\) nanoparticles, it provides an innovative idea that allows the localized annealing of the active layer without influencing the support. The magnetic treatment of Fe\(_3\)O\(_4\) nanoparticles could possibly adjust the MMM morphology by heat generation, which leads to acceleration of the thermal motion of the polymer. In terms of the organosilane family (such as PhTMS, DMDPS, APTMS etc.), the application of organosilane combined with polymer membrane in different schemes to optimize membrane performance have been extensively discussed. According to the study reported by Xia et al.\(^9\), the reaction tendency of each organosilane was determined by their molecular structure and the functional groups they possess, the organosilanes with phenyl group (such as PhTMS and DMDPS) are likely to generate silica particle via hydrolysis and self-condensation due to steric hinderance, the confirmation of reaction mechanism about various organosilanes have practical value for the post-modification of polymer membranes to improve membrane separation performance and long-term stability.

### 8.2 Future Work

Based on the work in this project, PIM-1 based thin film composite (TFC) membranes dramatically improves the flux of membranes to meet the demands for industrial application. However, the ability of PIM-1 membranes to recover butanol
from aqueous solution still has potential for further improvement. Additionally, control of membrane swelling is still a big issue which restricts the application in the industrial field. Therefore, future work is recommended to improve the butanol/water selectivity of TFC membranes, and the main focus is the optimization of the active layer, in which hydrophobic nanofillers blended with PIM-1 can be explored to accelerate the adsorption and diffusion of butanol molecules. Although graphene flakes have been confirmed as hydrophobic fillers and can improve the membrane flux, the sorption ability to butanol molecules is still limited. Therefore, the other exploration is a graphene-derivative, reduced graphene oxide (rGO), which is the mainly applied graphene-derivative. With the existence of carboxylic groups on rGO edge, it is possible to functionalize specific surfactants, which have similar solubility parameter with butanol molecules, on a graphene flake. Thus, using rGO flake as a carrier to prepare more hydrophobic nanofiller is expected to be an effective pathway for butanol recovery enhancement.

In terms of swelling control for PIM-1 membranes in pervaporation or nanofiltration processes, the design of a crosslinked structure is still the practical solution to a tight polymer structure and to prevent the swelling by butanol. The induction heating via Fe$_3$O$_4$ nanoparticles in PIM-1 membranes is worth further study. It should be noticed that neat PIM-1 membrane can only achieve cross-linking at extremely high temperature (350~400$^\circ$C in the presence of oxygen), this is extremely difficult to achieve within a PIM-1 matrix even if via magnetic treatment. Further study is recommended to incorporate a specific cross-linking agent into the PIM-1 matrix, that is blending a cross-linking agent and Fe$_3$O$_4$ nanoparticle together within PIM-1 matrix. It is expected that under the induction heating of Fe$_3$O$_4$ nanoparticles, the cross-linking agent may react with PIM-1 to form covalent bonds at a reasonable temperature (possibly below 200$^\circ$C). This scheme could be particularly effective for PIM-1 TFC membranes, in which a crosslinked structure in the PIM-1 active layer can be achieved, without affecting the PVDF support.
8.3 References


