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POLY(VINYLIDENE FLUORIDE) MEMBRANES

Submitted by

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Declaration of Originality

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and the relevant references are included in this thesis.

Jing Ji

Imperial College London

August 2016

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Abstract

Poly(vinylidene fluoride) (PVDF) membranes have been intensively investigated and commercialised with broad applications in water purification and wastewater treatment for decades due to its outstanding properties. Currently, PVDF membranes are mainly produced by the phase inversion technique, which is predominant in both laboratory research and industrial manufacturing. Various modification methods based on the phase inversion technique have also been developed to improve the membrane performances, but these improvements are incremental and there have been no important breakthroughs during the past decade.

This thesis first explores the preparation of reinforced PVDF flat sheet membranes by blending nanoclay followed by the phase inversion process. Although the membranes showed improved water permeation flux and enhanced abrasion resistance, further improvements are limited by the phase inversion technique itself. Consequently, a new concept of membrane manufacturing procedure has been proposed by combining unidirectional crystallisation of green solvent and polymer diffusion. The new method uses crystallites of a solvent dimethyl sulfoxide with controlled sizes as pore templates to create enormous nanosized flow passages. It follows a completely different pore formation mechanism and therefore overcomes the drawbacks of the phase inversion technique. The resultant PVDF membranes have an asymmetric structure composed of a highly porous separation layer and gradually opened micro-channels. Due to the unique structure, the prepared membranes showed excellent permeation performances and mechanical properties overwhelming commercial PVDF membranes prepared by the phase inversion technique. The filtration performance of the PVDF membranes can be further improved by modification of the membrane material, for example, by blending polyethylene glycol in the dope solution. The obtained membrane with pore size of 36 nm showed extraordinary high flux of 1711 L/m²h and could withstand 35 bar in the test. Moreover, the new manufacturing process is of much fewer influencing factors compared to the phase inversion approach and thus highly reliable and repeatable. In principle, it is also applicable to other common polymeric membrane materials such as polyethersulfone and cellulose acetate.

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Chapter 1 Introduction

1.1 Background

In recent years, water crisis has become an urgent global issue due to climate change, water pollution, wasteful use of water in agriculture and rapid population growth, and has hence attracted much attention from researchers and governments [1]. Among the various water treatment techniques, membrane separation technology has exhibited several advantages, such as low energy requirement because of no phase change, low capital investment and maintenance requirements, high process flexibility, simplicity and ease of installation and operation, low weight and space requirements [2]. Consequently, membranes have been widely used in water purification and wastewater treatment processes for decades mainly in the forms of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO).

According to Cheryan's study [3], membranes can be produced from more than 130 materials, among which only a few have been successfully commercialized. Membranes can be classified into two categories based on the nature of the material, i.e. organic (polymeric) membranes and inorganic membranes. Compared to inorganic membranes, polymeric membranes are more popular and have occupied a higher percentage of the membrane market, since polymeric membranes are normally cheaper. This is because they can be produced without high temperature treatment, which is normally required in the production of ceramic membranes. Commonly used commercialized polymeric membrane materials include cellulose acetate (CA), polyamide (PA), polyimide (PI), polysulfone (PS), polyethersulfone (PES), polypropylene (PP), polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVDF) and polytetrafluoroethylene (PTFE).

Among the above-mentioned materials, PVDF is one of the most commonly used MF/UF membrane materials due to its outstanding properties including chemical resistance [4], thermal stability [5] and excellent mechanical strength. Indeed, PVDF membranes have been widely applied in various separation processes including water/wastewater treatment such as drinking water production, pre-treatment for RO systems and wastewater treatment, membrane contactors such as gas-liquid absorption and membrane distillation, and some other applications [6]. As investigated by Bottino et al. [7], PVDF can be dissolved in several common organic solvents including N, N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), etc. The solubility of PVDF makes it possible to manufacture membranes by the simple and economical phase

inversion technique. In both laboratory research and industrial manufacturing, asymmetric and symmetric PVDF membranes are mainly fabricated by non-solvent induced phase separation (NIPS) method [8, 9] and thermally induced phase separation (TIPS) method [10-12], respectively.

Apart from the advantages mentioned above, PVDF membranes also face challenges in real practice. For example, PVDF membranes normally possess low permeance, which means that more membrane modules will be needed in order to treat large quantities of water, and thus increasing the capital investment and daily operating costs. The hydrophobic nature of PVDF also makes membrane fouling nearly inevitable especially when PVDF membranes are applied in the treatment of wastewater containing natural organic matters, e.g. proteins [13, 14]. Membrane fouling will cause a severe decline in flux and frequent cleaning steps are necessary to maintain the throughputs of the modules. Another issue is membrane wearing caused by the suspended particles compressing and grinding the membrane surface, which normally cannot be avoided and will compromise the stability and durability of PVDF membranes [15].

Regarding these disadvantageous properties of PVDF membranes, various modification techniques have been developed to improve membrane hydrophilicity, enhance membrane permeance and mechanical strength [8, 16]. Generally, there are two strategies to modify PVDF membranes, i.e. surface modification including surface coating, surface grating and blending modification employing enhancing additives such as hydrophilic polymers, amphiphilic copolymers and inorganic nanoparticles. In the surface modification process, a thin hydrophilic layer is either deposited on the membrane surface directly or connected to membrane surface by functional chains. While in the blending modification process, additives with desirable properties are introduced to the polymer dope solution followed by the phase inversion process to form modified membranes. The modification techniques based on the phase inversion process can effectively reduce the tendency of fouling and improve permeation flux. However, these improvements have been saturated during the past decade and further improvements are difficult.

In terms of membrane manufacturing at an industrial scale, hazardous solvents (DMAc and NMP) have been adopted in the production of PVDF membranes using the phase inversion technique in large quantities [17, 18]. The prepared membranes also have some structural drawbacks, such as macrovoids and a dense skin layer with low surface porosity. The former

will deteriorate the mechanical strength when membranes are used in high-pressure applications, whereas the latter is adverse to the membrane permeability.

Generally, a technological limit of the phase inversion technique has been reached, especially for the production of PVDF membranes, and there has been no significant breakthrough over the last decade in terms of new manufacturing procedures. New manufacturing techniques are required to produce membranes with high performances in an easily controlled and environmentally sustainable way.

In materials engineering, a simple approach of “freeze drying” is often employed in the production of porous materials [19-21]. This method utilizes solvent crystallites formed in the freezing step as templates to produce micron-scale pores in the material. A few attempts have been made to produce PVDF membranes via this approach but failed with the membrane pore size larger than 250 nm due to lack of effective control of the solvent crystallisation process [22, 23]. Nevertheless, the freeze drying method seems to be a promising approach for membrane manufacturing if the remaining issue of pore size control can be tackled.

1.2 Thesis Objectives

The overall objective of this thesis is to explore new membrane manufacturing processes that can bring breakthroughs to overcome current technological limits of the phase inversion technique. This thesis will focus on the PVDF membranes, considering their intensive usage in membrane filtration processes.

The initial attempt was still to prepare PVDF flat sheet UF membranes through the conventional phase inversion method to understand the structural features, performance and limitations of the phase inversion membranes. In this work, hydrophilic polyethylene glycol (PEG) and natural clay palygorskite (PGS) nanorods with varied loading amounts were added to the PVDF/triethyl phosphate (TEP) dope solution to produce modified PVDF membranes. Apart from essential structural and performance characterisations, a simple and quantitative methodology was proposed to assess the anti-wearing property of membranes.

The focus of this PhD study was then transferred to the development of a novel membrane preparation method by combining solvent crystallisation and polymer diffusion (CCD) based on a freezing technique. PVDF flat sheet membranes were produced via the CCD method using DMSO, DMAc and NMP as the solvent. According to the proposed mechanism, the effects of cooling rate, casting thickness and choice of solvent on the obtained flat sheet

membranes were investigated. Furthermore, for comparison purpose, samples were also prepared from the same dope solutions using the phase inversion technique and then the structure and performance of the two membranes were compared. Moreover, PEG was employed as an additive to further enhance the performance of the PVDF membranes prepared by the CCD method.

The specific objectives of this thesis are summarised as follows:

1.2.1 PVDF/Palygorskite Composite Ultrafiltration Membranes with Enhanced Abrasion Resistance and Flux

- 1) To prepare PVDF flat sheet membranes using TEP as the solvent, PEG and PGS as the additives by combination of NIPS and TIPS methods;
- 2) To characterise the morphologies, filtration performances and transport properties of the obtained membranes;
- 3) To investigate the effect of varied PGS loading amounts on the resultant membranes;
- 4) To establish a feasible and reliable testing protocol for analysing the abrasion resistance of a membrane sample in the laboratory.

1.2.2 Formation of Porous PVDF Membranes via the Combined Solvent Crystallisation and Polymer Diffusion Technique

- 1) To propose a new CCD manufacturing procedure for the production of polymeric membranes with high performance in an environmentally sustainable way;
- 2) To prepare PVDF flat sheet membranes using the proposed CCD method, followed by a series of structural characterisations;
- 3) To study the effect of various parameters involved during the CCD process on the structure of prepared membranes, including cooling rates, casting thicknesses and the solvent types.

1.2.3 Permeation Characteristics and Mechanical Properties of the PVDF Membranes Prepared by the CCD Technique

- 1) To prepare PVDF flat sheet membranes using both the newly developed CCD method and conventional NIPS method with DMSO, DMAc and NMP as the solvent;
- 2) To investigate the structural and performance characteristics as well as mechanical properties of the resulting membranes and then compare to some commercial PVDF membranes;

- 3) To make a comprehensive comparison between the CCD method and the NIPS method regarding the production of flat sheet membranes.

1.2.4 Enhancement of CCD PVDF Membranes by Blending PEG

- 1) To prepare PVDF/PEG blend membranes with PEG as a hydrophilic additive via the CCD method;
- 2) To characterise the structure, performance and properties of the prepared PVDF/PEG blend membranes;
- 3) To study the effect of PEG addition on the prepared membranes and compare to pure PVDF membranes prepared by the CCD method and commercial PVDF membranes prepared by the NIPS method.

1.3 Thesis Structure and Organisation

This thesis consists of seven main chapters. **Chapter 1** provides an overview of the whole thesis and specific objectives in each part of the work. **Chapter 2** first describes the intrinsic properties of PVDF material and summarises current applications of PVDF membranes. The predominant preparation techniques and numerous modification methods of PVDF membranes are then discussed in details. The technical limit of the most commonly used phase inversion method is then pointed out, followed by an introduction of the “freeze drying” approach, which shows great potential in membrane production. **Chapter 3** describes the preparation of PVDF flat sheet membranes with PEG and PGS as the additives via the conventional phase inversion technique. The effects of varied PGS loading amounts on the obtained membranes are investigated. In particular, a simple and quantitative method is established to analyse the membrane abrasion resistance reliably. In **Chapter 4**, a novel membrane preparation technique is developed to prepare high-performance membranes by combining solvent crystallisation and polymer diffusion. Based on the proposed mechanism, the effects of various parameters including cooling conditions, casting thickness and solvent nature on the prepared membranes are investigated. **Chapter 5** describes the preparation and characterisation of PVDF membranes prepared by the CCD method and the NIPS method. Differences between the two kinds of laboratory-produced PVDF membranes and some commercial PVDF membranes prepared by the NIPS technique are discussed in order to make comprehensive comparisons between the newly developed CCD method and conventional NIPS method. **Chapter 6** describes the fabrication of PVDF/PEG blend membranes via the CCD method. The membrane morphology, performance and properties of the blend membranes are studied and compared to pure PVDF membranes prepared by the CCD

technique as well as commercial PVDF membranes prepared by the NIPS technique. **Chapter 7** summarises the conclusions drawn from the research work discussed in Chapters 3 – 6 and also provides recommendations on the future work.

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Chapter 2 Literature Review

2.1 Introduction

Water shortage has become a global concern due to increasing population, drought occurrences and contamination of drinking water. It has triggered numerous research works focusing on the purification of groundwater and recovery of pure water from wastewater or polluted groundwater streams. Among the various separation techniques developed, membrane technology is recognized as one of the most effective approaches for water/wastewater treatments. Membrane filtration is a separation process based on size exclusion through a porous media, i.e. a membrane. In the filtration process, fluids and smaller particles pass through the pores while larger particles are rejected. Porous membranes have been widely used in liquid filtration for drinking water production, wastewater treatment, dialysis, beverage clarification, etc. Membrane-based filtration is now a business worth tens of billions USD per year, among which microfiltration (MF, pore size > 100 nm) and ultrafiltration (UF, pore size ranging from 2 to 100 nm) share the biggest part of the total membrane market.

The importance of poly(vinylidene fluoride) (PVDF) as a membrane material has long been recognized in many membrane processes. Particularly, PVDF is one of the most commonly used among all the MF/UF membranes materials. PVDF is a semi-crystalline polymer with the repeating unit of $-\text{CH}_2-\text{CF}_2-$ containing 59.4 wt.% fluorine and 3 wt.% hydrogen. In the industrial manufacturing process, PVDF is synthesised by emulsion polymerization or suspension polymerisation of 1,1-difluoroethene, $\text{CH}_2=\text{CF}_2$ [1]. There are many commercial PVDF materials available in the market, as summarized by Massey [2]. Generally, Atofina Kynar produces PVDF granules and powders, whereas Solvay Solef provides homopolymers with high crystallinity like Ausimont Hylar MP Series, and copolymers with high flexibility like Hylar FX and FXH Series. Regarding membrane fabrication, Arkema Inc. (or previously known as Atofina Chemicals Inc. or Elf Atochem) and Solvay are the two major commercial PVDF material suppliers in the world.

Compared to other polymeric membrane materials, PVDF has received great attention due to its outstanding inert material nature. PVDF exhibits high mechanical and impact strength, which are affected by its crystallinity ranging between 35% and 70%. The crystallisation of PVDF is influenced by various parameters including polymerisation method, molecular weight, molecular weight distribution, thermal history and cooling rates [3]. In addition, unlike most

crystalline polymers, PVDF is thermodynamically compatible with other polymers including PMMA over a wide range of blend compositions [4].

Similar to other fluoropolymers, PVDF is normally stable under thermal environments due to the high electronegativity of fluorine atoms and the high bond dissociation energy of the C–F bond. It has been reported that PVDF membranes can withstand prolonged exposure to high temperatures of 366K [5] and can be autoclaved for sterilised applications (typically at 394K). However, discolouration of PVDF has been observed at high temperatures, which suggests the occurrence of thermal degradation. Relevant studies indicate that PVDF is thermally degraded predominantly by the removal of HF, namely dehydrofluorination, followed by the formation of C=C double bond or cross-linking, as shown in Figure 2.1 [6].

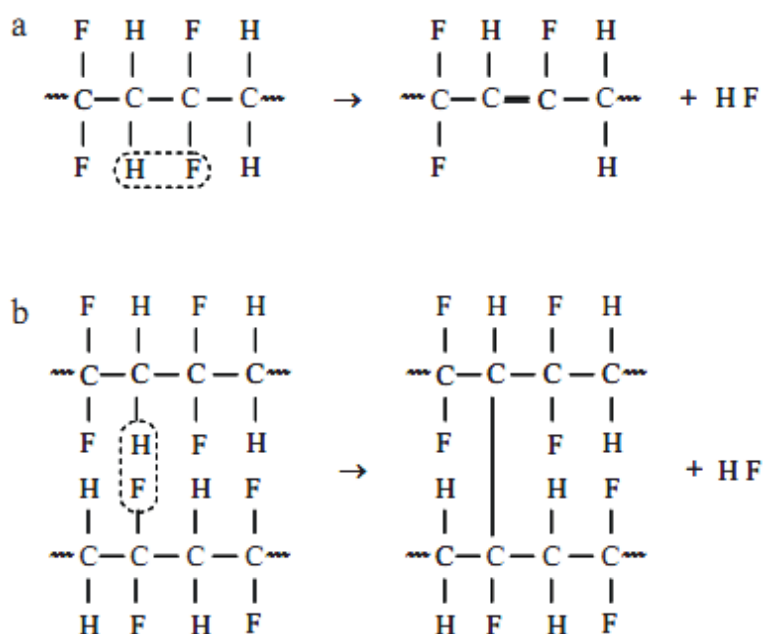


Figure 2.1 Schematic diagram of the mechanism of dehydrofluorination in PVDF and (a) formation of double bonds in the chain and (b) cross-linking of the polymer [6]

PVDF also has the characteristic resistance of fluoropolymers to most chemicals and solvents, such as halogens and oxidants, inorganic acids, as well as aliphatic, aromatic and chlorinated solvents [7]. In particular, PVDF can survive from chlorination disinfection, which makes it dominant in the pre-treatment units of seawater desalination plants and in wastewater treatments. However, PVDF is defenceless in the caustic environment. Degradation of PVDF with discolouration from white to brown and finally black has been observed, as well as the decrease of membrane mechanical strength [8-10]. This phenomenon is attributed to the dehydrofluorination of PVDF, as shown in Figure 2.2. The formation of carbon-carbon double and triple bonds due to the loss of HF has been verified by FTIR [11, 12] and UV-vis

spectroscopy [13]. Hashim et al. conducted a systematic investigation of the stability of PVDF hollow fibre membranes in NaOH solutions with different concentrations at both low and high temperatures [14]. The results suggested that the reaction between PVDF and NaOH started at low NaOH concentrations and was further accelerated by extended treatment time, increased NaOH concentration and treatment temperature.

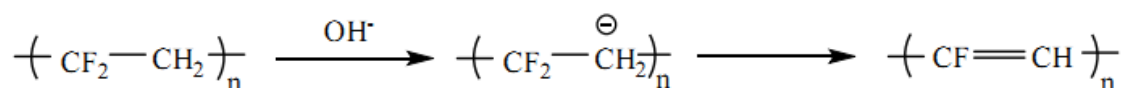


Figure 2.2 Schematic of reaction between PVDF and NaOH

In addition, the solubility behaviour of PVDF in 46 liquids has been investigated by Bottino et al. [15]. The authors suggested that PVDF could be dissolved in eight solvents including *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), hexamethyl phosphoramide (HMPA), tetramethylurea (TMU), triethyl phosphate (TEP) and trimethyl phosphate (TMP). This means that it is possible to produce PVDF membranes by a simple and cheap phase inversion technique, which is one of the most common industrial processes in large-scale membrane manufacture. The preparation of PVDF membranes will be discussed in details in Section 2.2.

These properties coupled with its intrinsic hydrophobicity have made PVDF a popular membrane material in many membrane processes [16]. Nowadays, PVDF membranes have occupied a large percentage of the commercial MF and UF membrane market. PVDF MF membranes are normally used as a part of the membrane bioreactor (MBR) or in the upstream of water treatment processes. On the other hand, the UF membrane market is almost dominated by PVDF membranes in three key applications, i.e. water purification in potable water plants, pre-treatment in desalination plants and wastewater recovery for industrial applications. Numerous commercial PVDF membrane products have been developed by various manufacturers, such as Pentair X-Flow, General Electric Water & Process Technologies, Evoqua Water Technologies (previously Siemens Memcor), Asahi Kasei Chemicals Corporation, Hyflux, Toray Membrane, Koch Membrane Systems, etc. Moreover, PVDF has been recognised as a suitable membrane material for membrane contactor applications [17, 18] and much effort is currently being devoted to the preparation of PVDF membranes with improved morphology and properties for membrane distillation [19] and absorption or removal of gases such as CO₂ [20] and H₂S [21] from flow streams. Despite the broad commercial application in water and wastewater treatments and extensive study in the application of

membrane contactors, PVDF membranes have also been investigated for other applications such as support material, bioseparation and biotechnological applications.

2.2 Preparation of PVDF Membranes

To date, many techniques have been developed to prepare membranes for separation processes, such as sintering, controlled stretching, track-etching, electrospinning and phase inversion. Generally, the selection of a proper preparation method is based on the material used and the desirable membrane structure.

In the sintering method, material powders are compressed and then sintered below its melting temperature. The prepared membranes always possess irregular pores with low porosity and wide pore size distribution. Moreover, sintering is commonly used to prepare membranes made from materials that have poor solubility in normal solvents, such as ceramic materials.

In the controlled stretching method, a semi-crystalline polymer melt is extruded or spun followed by drawing, annealing, and finally stretching. During the very fast drawing process, the lamellar crystallites in the polymer are aligned in the drawing direction, which is perpendicular to the direction of stretching. Then in the stretching process, pores and voids are formed by rupturing the amorphous region of the polymer, whose crystalline region gives the mechanical strength of the resulted membrane.

In the track-etching process, a polymer film is subjected to high-energy radiation applied perpendicular to the film, which results in tracks with a certain diameter. Then the “damaged” polymer film is immersed into the etching bath composed of alkali or acid, which reacts with damaged polymer chains in the track. Consequently, microporous membranes with very uniform, almost perfectly round cylindrical pores can be obtained via the track-etching method. However, such membranes always have low porosity and are very expensive.

Compared to other membrane preparation methods, electrospinning is a relatively newly developed technique. In the electrospinning process, fibres in sub-micro to nano-scale are created from a polymer solution or melt through an electrically charged jet and form a conical shape under the electric field [22]. The ejected nanofibres overlap randomly forming a membrane with an ideal open porous structure. The electrospun nanofibrous membranes have several outstanding properties, such as high porosity, high permeability and large surface area.

However, electrospun membranes require additional support to provide membrane mechanical strength in real practice [23].

Indeed, commercial polymeric MF/UF membranes are mainly produced by the phase inversion technique due to its simplicity, flexible production scale and hence, low cost [24]. As discussed in the previous section, the solubility of PVDF in common organic solvents makes it possible to prepare PVDF membranes by the phase inversion method. In the phase inversion process, a homogeneous polymer solution is converted into membranes with the desirable geometry in a controlled manner. Generally, the phase inversion could be triggered by several methods leading to different techniques, such as solvent evaporation, precipitation by controlled evaporation, precipitation from vapour phase or vapour induced phase separation (VIPS), thermal precipitation or thermally induced phase separation (TIPS), and immersion precipitation or non-solvent induced phase separation (NIPS) [25]. All the phase inversion processes lie on the same thermodynamic principle, which start from a thermodynamically stable solution followed by demixing. Although some commercial membranes are produced by TIPS method [26-28], nowadays, NIPS is the predominant manufacturing process for PVDF membranes in industrial scales [24, 29]. These two phase-inversion techniques will be discussed in details in the following sections.

2.2.1 Thermally Induced Phase Separation

Thermally induced phase separation is usually employed to produce microporous membranes with controlled structures from a wide range of crystalline and thermoplastic polymers including PVDF. In the TIPS process, the conversion of a homogeneous solution into a two-phase mixture is conducted by removing the thermal energy. The polymer is first dissolved or melt-blended in a high-boiling-point low-molecular-weight liquid or solid, named diluent, to form a homogeneous solution, which is then cast or spun into desirable shapes and cooled in a quenching process. As a result, phase separation and solidification of the polymer are induced and membranes with a microporous structure are obtained after the diluent is removed [26].

2.2.1.1 Mechanism of TIPS

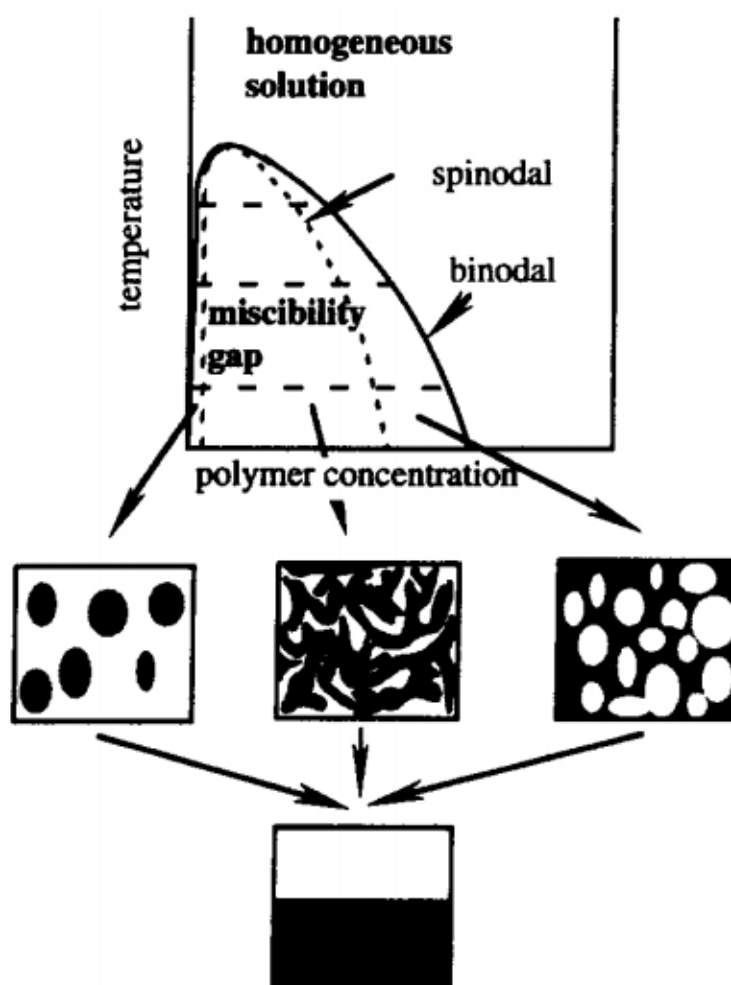


Figure 2.3 Schematic phase diagram of a binary polymer-solvent system [30]

In order to investigate the mechanism of the liquid-liquid demixing process in the TIPS process, a phase diagram of a binary system composed of polymer and solvent is represented in Figure 2.3 [30]. The polymer solution is homogeneous and thermodynamically stable at high temperatures. As the temperature decreases, the solution starts to demix into two liquid phases, i.e. polymer-lean phase and polymer-rich phase. This is referred to as liquid-liquid demixing and the liquid-liquid phase boundary is so-called the binodal. Each of the horizontal tie lines in the figure connects two points on the binodal curve, which are the compositions of two co-existing phases in equilibrium with each other since they have the same chemical potential. The region under the binodal is called miscibility gap; the curve under the binodal is named as spinodal; the composition at which the binodal and the spinodal coincide is defined as critical point. Polymer solutions with compositions located in the region between the binodal and the spinodal are metastable, which means that the solutions are stable with small fluctuations in the composition. In other words, if the composition of the polymer solution is smaller than that

of the critical point, nucleation and growth of small droplets of the polymer-rich phase take place and the droplets are dispersed in the polymer-lean phase after liquid-liquid demixing. When the solution composition is larger than that of the critical point, small droplets of the polymer-lean phase are dispersed in the polymer-rich phase after liquid-liquid demixing. However, the solution within the spinodal curve is thermodynamically unstable and even very small fluctuations in the composition will cause spontaneous phase separation, which is called spinodal demixing.

The composition paths representing the composition change in the binary system are also illustrated in Figure 2.3 and have been studied to understand the mechanism of liquid-liquid demixing in the TIPS processes and to predict the morphology of the resultant membranes. Basically, there are three different composition paths resulting in the formation of membranes with three different structures. When the polymer solution is dilute with a small polymer concentration (left path), as the temperature decreases, liquid-liquid demixing occurs once the binodal curve is attained and nuclei of the polymer-rich phase are formed and grow further till the thermodynamic equilibrium is reached. As a result, membranes with a latex structure and unsatisfactory mechanical strength will be obtained. On the other hand, when the original concentration of the polymer solution is high (right path), liquid-liquid demixing takes place by nucleation and growth of the polymer-lean phase dispersed in the polymer-rich phase. In this case, membranes with open porous structure will be prepared if the droplets of the polymer-lean phase grow large enough and connect with each other before the surrounding polymer-rich phase solidifies. Otherwise, the resultant membrane will have a cellular structure composed of closed pores. Besides, when the polymer composition reaches the spinodal curve, spinodal demixing takes place and both liquid phases are mixed with each other and completely interconnected (centre path). Consequently, membranes with an interconnected bicontinuous structure and high permeability will be produced.

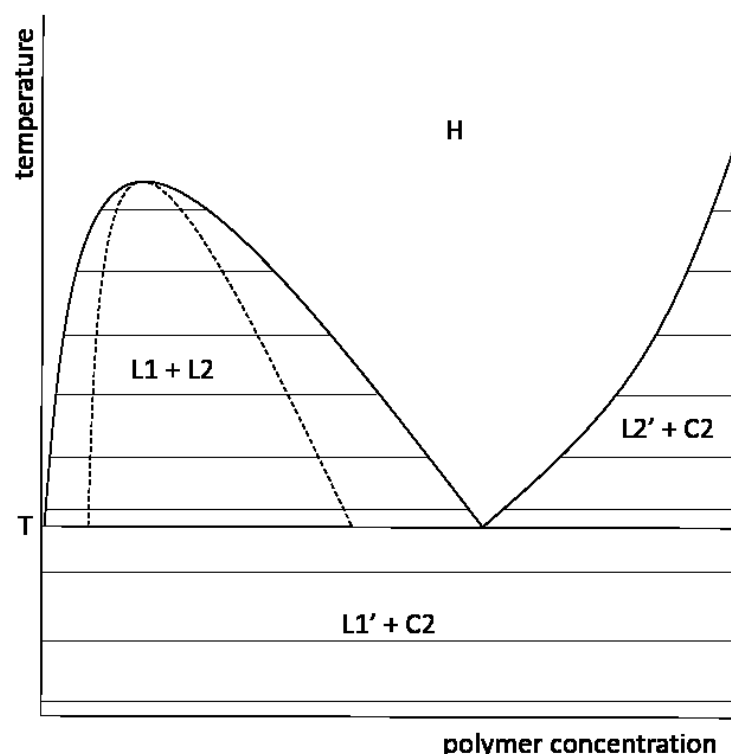


Figure 2.4 Schematic phase diagram of combined liquid-liquid demixing and polymer crystallisation (adapted from [30])

The composition paths discussed above and their corresponding structures of the resultant membranes are based on liquid-liquid demixing. However, crystallisation of PVDF may also cause the solidification of the polymer in the phase inversion process since PVDF is a semi-crystalline polymer and crystallises rapidly. The solid-liquid demixing should therefore be included in the study of the formation mechanism of PVDF membranes in the TIPS process. In some cases, when the temperature of the polymer solution is decreased to a certain value, the polymer-rich phase is stabilised and solidified through polymer crystallisation and the membrane morphology is formed from solid-liquid demixing. In some other cases, liquid-liquid demixing and polymer crystallisation can take place simultaneously. Figure 2.4 schematically shows the phase diagram of combined liquid-liquid demixing and polymer crystallisation [30]. In the figure, H represents the homogeneous solution at high temperatures. If the polymer solution is dilute, liquid-liquid demixing happens as the temperature decreases and equilibrium of the dilute polymer solution (liquid phase 1, L1) and the concentrated polymer solution (liquid phase 2, L2) is achieved. If the polymer solution is concentrated, solid-liquid demixing occurs while decreasing the temperature, which results in concentrated polymer solution (liquid phase 2', L2') and polymer crystallites (C2) being in equilibrium. There is also a region in the figure where the dilute polymer solution (liquid phase 1', L1') is

in equilibrium with polymer crystallites (C2). There is a specific temperature (T) at which the three phases are in equilibrium with each other. Thus, different phase separation process can occur based on the composition of the polymer solution and the cooling rate, and thus membranes with various structures can be produced.

2.2.1.2 Influencing Factors of TIPS

Generally, the formation of PVDF microporous membranes by TIPS method undergoes solid-liquid demixing with a typical spherulite morphology obtained [26, 31, 32], although liquid-liquid demixing may be induced in some cases [33]. The type of phase separation behaviour is affected by the interaction between the polymer and the solvent or diluent, which has generated considerable investigations on the selection of a proper diluent or diluent mixture [28, 31, 34-36]. For example, Gu et al. prepared PVDF membranes via TIPS method from 4 different diluent mixtures and found that the use of a diluent having close polarity to PVDF favoured the flow and congregation of polymer-rich phase, which led to the formation of a discernible spherulitic structure [28]. Their study implied that as the interaction between the polymer and diluents decreased, the obtained spherulitic structure became less discernible and the membrane porosity increased. In addition, the effects of various compositions of the diluent mixture on membrane morphology were investigated by Li et al. [34]. The results suggested that the ultimate membrane structure could vary from large spherulitic morphology to bicontinuous interconnected morphology by adjusting the ratio of the two components in the diluent mixture, which affected the demixing mechanism in the phase separation process. Similar results had been obtained by Ji et al. [35].

In the solid-liquid demixing process, phase inversion is induced by nucleation and growth of PVDF crystallites from a concentrated polymer solution [26]. This mechanism is achieved by cooling the polymer solution in a quenching process, which means that the quenching conditions, such as the cooling rate, the temperature, and the composition of the quenching bath also influence the phase separation process and the ultimate membrane morphology. Generally, when quenching at low temperatures, the high cooling rate promotes the crystallisation rate of PVDF, thus membranes with numerous small spherulites and small interspherulite voids (channels of open pores throughout the membrane cross section) will be produced [31]. Some research works have found that increasing the quenching temperature led to the formation of larger spherulites with more regular shape [28, 37, 38]. In Cui and co-workers' work using sulfolane as the diluent, however, completely different results were

obtained suggesting that the shape of the spherulites produced at lower quenching temperatures were more uniform [32].

Moreover, inorganic nanoparticles have been added to the dope solution in order to modify the phase inversion process and thus the ultimate membrane structure and properties. Different particles have different influences on the TIPS process. For instance, Li and Lu compared the morphology of PVDF membranes prepared with and without CaCO_3 addition [39]. It was found that the presence of CaCO_3 interfered the polymer crystallisation at low quenching temperatures and also had a negative effect on the tensile strength of the prepared PVDF membranes. Cui et al. employed micro-sized SiO_2 particles in the preparation of PVDF blended membranes via TIPS method [40]. The characterisation results indicated that the introduction of the micro-sized SiO_2 particles had an adverse effect on the formation of PVDF spherulites but enhanced the membrane porosity, permeability and tensile strength. Shi et al. studied the differences in the morphological and crystalline properties of a pure PVDF membrane and PVDF- TiO_2 hybrid membranes [38]. They found that the growth of PVDF crystallites was affected by agglomeration and heterogeneous nucleation of TiO_2 nanoparticles. At low quenching temperatures, the prepared hybrid membranes consisted of more uniform and smaller spherulites compared to the neat PVDF membranes. That was because the TiO_2 nanoparticles played a role of nuclei in the crystallisation process of PVDF. However, when increasing the quenching temperature to more than 60 °C, the formation of polyhedral spherulites was observed and the growth of (0 2 0) plane of PVDF was suppressed.

Besides, many investigations have been conducted to study the effects of other preparation conditions on the phase separation process of PVDF in the TIPS process and the resultant membrane morphology, such as non-solvent concentration and water bath temperature [41], polymer concentration [36, 42], dissolving temperature [43], blending with other polymeric additives [44] in the dope solution, etc.

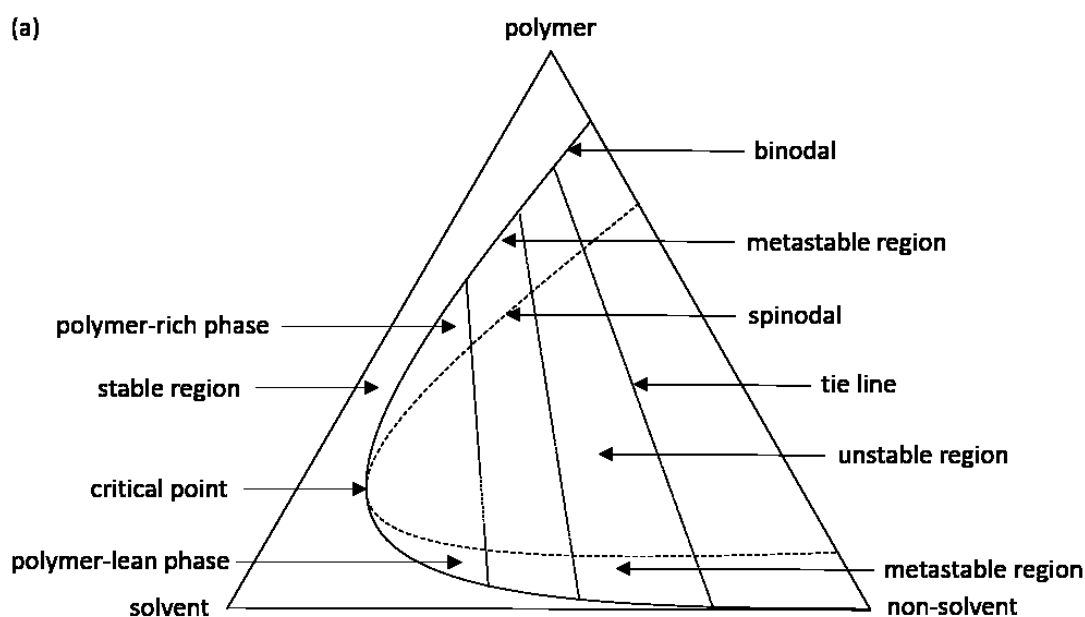
2.2.2 Non-Solvent Induced Phase Separation

As mentioned before, commercial PVDF membranes are manufactured disproportionately by non-solvent induced phase separation. In the NIPS process, a polymer solution is cast on a suitable support or spun as hollow fibres, followed by immersion in a coagulation bath composed of a non-solvent for the polymer. Then, the polymer precipitates forming membranes normally with an asymmetric structure. Phase inversion takes place due to the exchange of the solvent in the polymer solution with the non-solvent in the coagulation

bath. Consequently, the obtained membrane structure is affected by both mass transfer and phase separation.

2.2.2.1 Mechanism of NIPS

Compared to the binary system of polymer and solvent in the TIPS process, phase inversion in the NIPS process is more complicated since it involves at least three different components, i.e. polymer, solvent and non-solvent. For the sake of simplicity, only three components are taken into consideration when studying the phase separation mechanism and the NIPS process is regarded as an isothermal process [30]. The schematic phase diagram of a ternary system composed of polymer, solvent and non-solvent is illustrated in Figure 2.5(a). Each corner of the triangle represents one pure component; points on each side denotes the mixture of two corresponding corner components; any point inside the triangle stands for a mixture of three components. Like binary phase diagram, binodal, spinodal, critical point and tie lines can be observed in the ternary phase diagram.



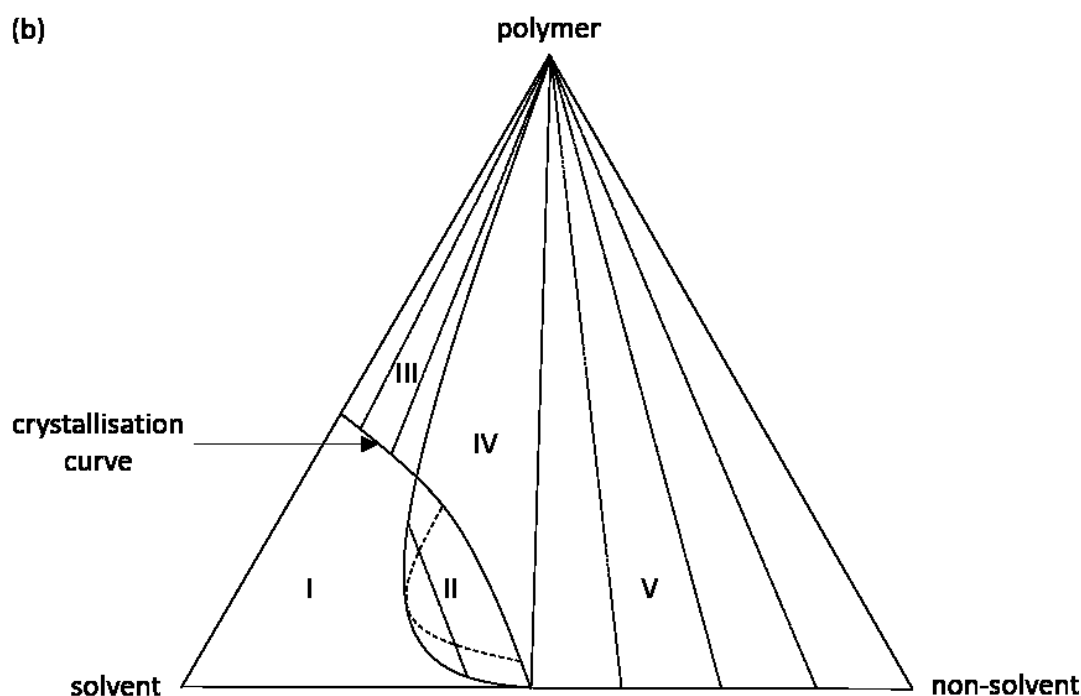


Figure 2.5 Schematic phase diagrams of a ternary system composed of solvent, non-solvent and (a) polymer and (b) semi-crystalline polymer (adapted from [25])

Similar to the TIPS process, crystallisation of PVDF in the phase separation process also needs to be taken into account in the NIPS process. Figure 2.5(b) displays the schematic phase diagram of a ternary system of a semi-crystalline polymer, solvent and non-solvent. In **Region I**, all the three components are in equilibrium forming a homogeneous and thermodynamically stable solution. In **Region II**, liquid-liquid demixing takes place without interference from solid-liquid demixing. In **Region III**, solid-liquid demixing occurs with polymer crystallising from the concentrated polymer solution. In **Region IV** where the liquid-liquid demixing gap and the solid-liquid demixing gap are overlapped, one solid phase and two liquid phases are in equilibrium. In **Region V**, the equilibrium of polymer crystallites and the polymer-lean phase is achieved. It should be noted that semi-crystalline polymers sometimes exhibit very low crystallinity in the final membrane since membrane formation is too fast to allow polymer crystallisation at a relatively slow rate. In this case, polymers undergo another solidification process, i.e. gelation, which is normally initiated by the formation of microcrystallites [25]. The microcrystallites are the polymer nuclei formed in the initial stage of the crystallisation process but cannot grow any further. In the gelation process, various polymer chains are connected together by these microcrystallites forming a three-dimensional network.

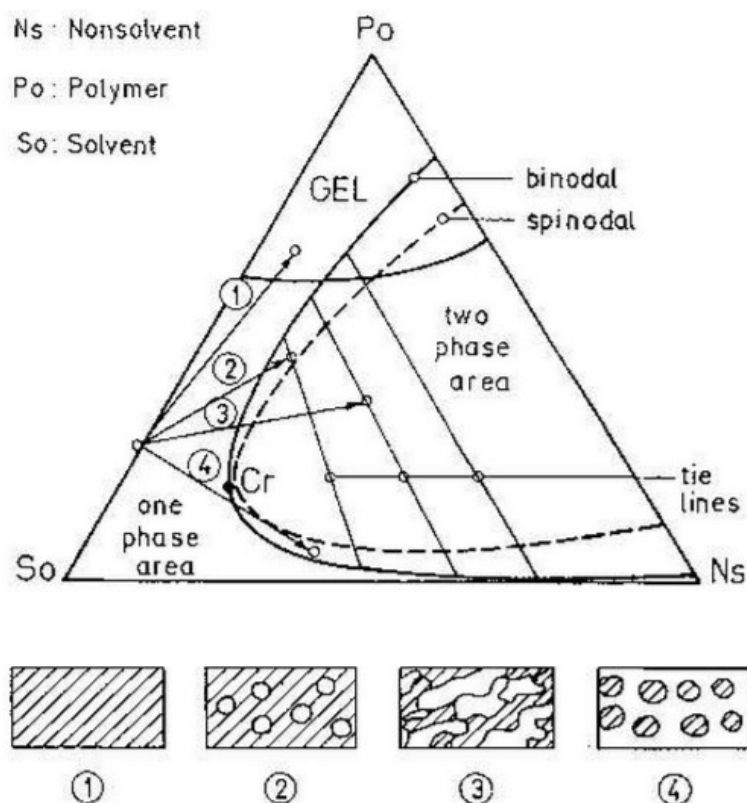


Figure 2.6 Ternary phase diagram of a polymer/solvent/non-solvent system with directions of distinguished composition paths [45]

For a better understanding of the membrane formation mechanism in the NIPS process, four different composition paths are represented in Figure 2.6 [45]. In the NIPS process, the phase inversion generally starts from a homogeneous solution with low polymer concentration. In **Composition Path 1**, the viscosity of the ternary system increases with increased polymer concentration since the out-flow of solvent into the coagulation bath is faster than the in-flow of the non-solvent into the polymer solution. Then, a sol-gel transition will be involved leading to the formation of a dense and compact structure. In **Composition Path 2**, the binodal curve is reached at compositions above the critical point, which results in liquid-liquid demixing accompanied by nucleation and growth of the polymer-lean phase. The droplets of polymer-lean phase are dispersed in the polymer-rich phase and can grow further until the surrounding polymer precipitates and solidifies. Normally membranes with cellular structure will be obtained in this case. However, an open porous structure may be formed if the droplets of polymer-lean phase coalesce. In **Composition Path 3**, spinodal demixing occurs as the spinodal curve is reached and the system is thermodynamically unstable. Both phases are continuous and are growing gradually and slowly. Finally, membranes with interconnected bicontinuous structure will be obtained. In **Composition Path 4**, liquid-liquid demixing and

nucleation and growth of the polymer-rich phase take place since the metastable miscibility gap is entered at compositions below the critical point. Theoretically, polymer latex will be obtained through this path. However, if the droplets of polymer-rich phase grow large enough and stick to each other before solidification, compact membrane structure will be formed. Thus, the membrane formation mechanism can be managed by controlling the NIPS process resulting in membranes with desirable morphology.

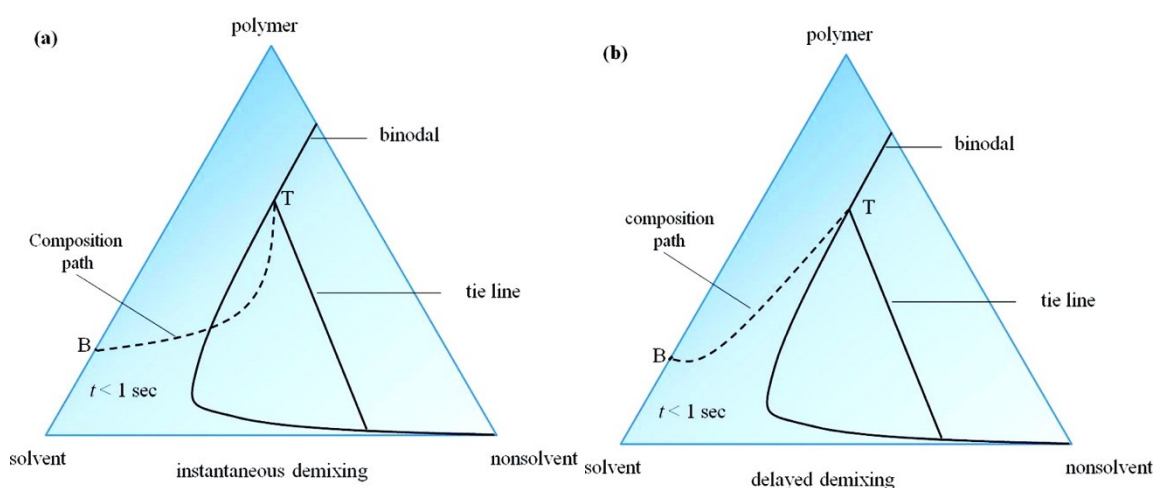


Figure 2.7 Schematic composition paths of the casting film immediately after immersion (T means the top surface of the film and B represents the bottom surface) [29]

As mentioned previously, the structure of membranes prepared via NIPS method is influenced by both mass transfer and phase separation. The demixing process can be classified into two types based on the time when demixing starts [25, 29]. In the instantaneous demixing process (Figure 2.7 (a)), the composition path crosses the binodal curve, which means that liquid-liquid demixing occurs immediately after immersion. As a result, polymer precipitates rapidly and asymmetric membranes with a relatively porous top surface and finger-like voids in the supporting layer are formed. Such membranes can be applied in microfiltration and ultrafiltration processes. On the other hand, in the delayed demixing process (Figure 2.7 (b)), all compositions throughout the polymer film lie outside the miscibility gap except the top surface. In this case, demixing will not take place until the composition path moves and crosses the binodal after a time interval. Consequently, membranes with a comparatively dense top layer and sponge-like structure in the supporting layer are obtained and are applicable in the gas separation and pervaporation processes.

2.2.2.2 Influencing Factors of NIPS

As described in the previous section, the ultimate membrane morphology is determined by both mass transfer and phase separation, which are affected by the thermodynamic and

kinetic properties related to various parameters involved in the membrane preparation process. Numerous research works have been conducted aiming to understand how the different parameters affect the membrane structure, performance and properties, which will be reviewed in this section.

2.2.2.2.1 Choice of Solvent

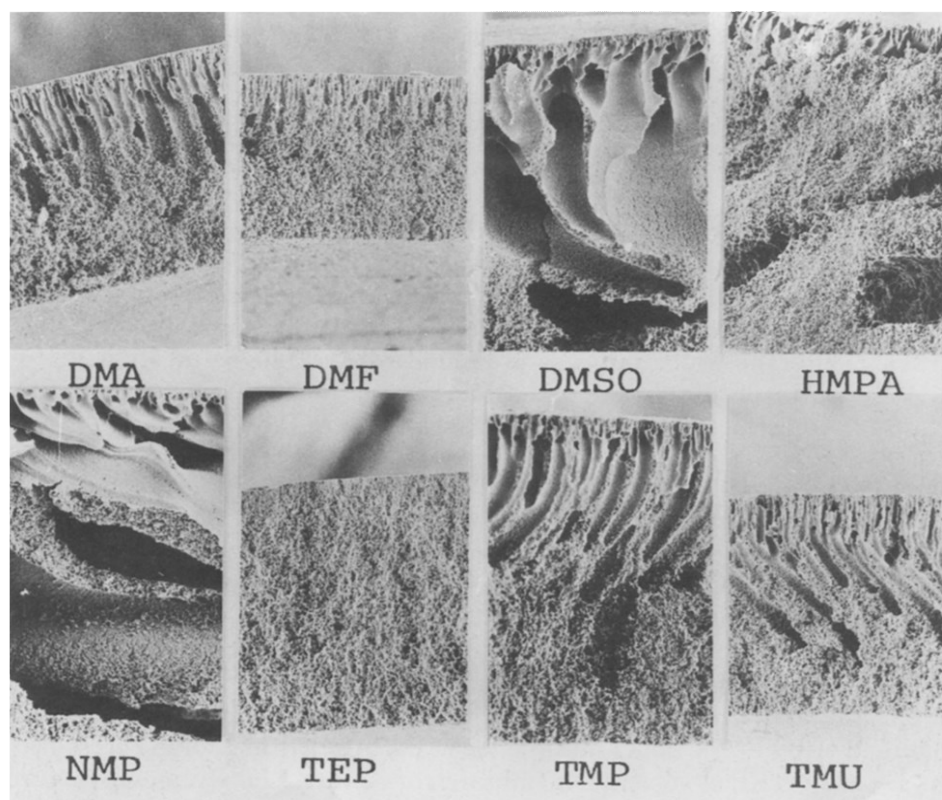


Figure 2.8 SEM images of cross-sections of membranes cast from 15 wt.% PVDF solutions in eight different solvents [46]

The selection of a proper solvent is of crucial importance in determining the ultimate membrane structure and performance targeting at a specific filtration process. Bottino et al. investigated the solubility behaviour of PVDF in 46 liquids and suggested that PVDF could be dissolved in eight solvents including DMAc, DMF, NMP, DMSO, HMPA, TMU, TEP and TMP [15]. The researchers then prepared microporous PVDF flat sheet membranes using the eight solvents and the morphology of the obtained membranes are shown in Figure 2.8 [46]. In their work, various properties such as solubility parameters of polymer, solvent and non-solvent, polymer-solvent compatibility, the cloud point, excess enthalpy of mixing, dope viscosity and solvent/non-solvent diffusivity were evaluated and poor dependence of these properties was built on the membrane performance. On the contrary, the authors suggested that

the mechanism of the membrane formation process was determined by diffusion and the membrane structure was in good correlation with the solvent/non-solvent mutual diffusivity.

In another work, Yeow et al. prepared PVDF membranes using four different solvents, i.e. DMAc, DMF, NMP and TEP, which were evaluated in terms of solvent power [47]. The polymer precipitation curve in each solvent system with water as the non-solvent was represented in a ternary phase diagram, as shown in Figure 2.9. Generally, a larger homogeneous region means more non-solvent needed to induce phase separation, which indicates stronger solvent power. Therefore, the power of four solvents could be ranked in the order of DMAc > NMP > DMF > TEP according to Figure 2.9. The cross-sectional structures of the four membranes were also observed under SEM [48]. Similar to Bottino's findings, membranes prepared with NMP had an asymmetric structure with irregular-shaped macrovoids underneath the skin layer, whereas using DMAc and DMF as the solvent led to the formation of asymmetric membranes composed of a thin skin layer with short finger-like voids underneath supported by a sponge-like structure. Furthermore, membranes prepared with TEP had a symmetric sponge-like structure without macrovoids, which was attributed to the weak solvent power of TEP and its weak affinity with water. The former character makes it possible to induce phase separation with a tiny amount of water, hence liquid-liquid demixing occurred at an early stage preventing the formation of macrovoids. While the latter character facilitates the formation of sponge-like structure.

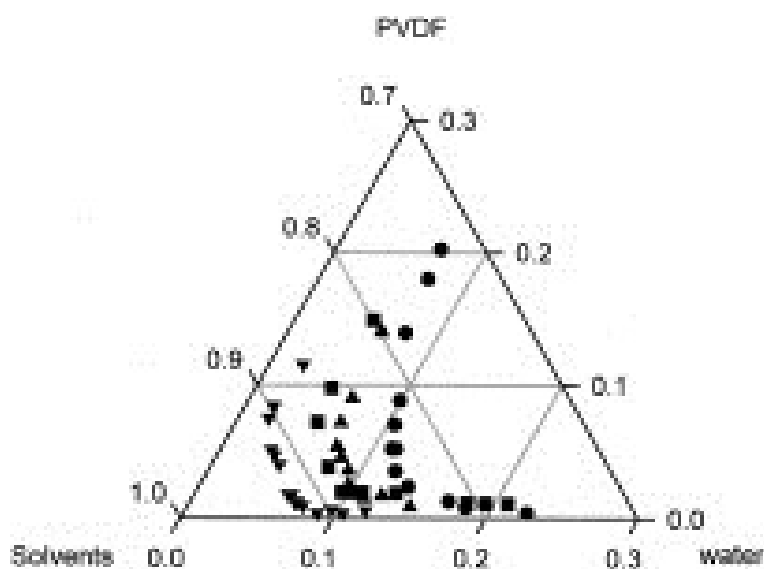


Figure 2.9 Isothermal phase diagram for PVDF Kynar 760/solvent/water ternary system at 25 °C (●DMAc; ▲NMP; ■DMF; ▼TEP) [47]

Li et al. studied the effects of mixed solvents on the morphology and performance of PVDF microporous membranes [49]. In their work, four pairs of mixed solvents were used including TMP-DMAc, TEP-DMAc, tricresyl phosphate (TCP)-DMAc and tri-*n*-butyl phosphate (TBP)-DMAc. The results showed that stronger solvent power to PVDF brought about faster polymer precipitation rate and less membrane shrinkage and thus the formation of membranes with higher flux. For instance, the flux of the membrane prepared with TMP-DMAc was 2.89 times that of the membrane cast with DMAc only and was 3.36 times that of the PVDF/TMP membrane. Compared to the strong solvent mixture of TMP and DMAc, the use of TEP-DMAc mixed solvents generated membranes with shorter finger-like voids beneath the skin layer and fewer macrovoids, which enhanced the membrane mechanical properties.

2.2.2.2.2 Dope Solution

In the NIPS process, phase separation starts from a homogeneous polymer solution, which is the dope solution. The phase inversion process and the resultant membrane morphology and properties are therefore affected by the parameters of the dope solution. For example, as the polymer concentration increased, the polymer solidification rate would be increased, which would suppress the formation of macrovoids and reduce the membrane porosity and pore size [50].

In Li's work [49], different commercial PVDF polymers were employed to prepare PVDF microporous membranes and to study the effects of polymer type on the phase separation process and the ultimate membrane properties. It was found that the type of PVDF homopolymer could affect the viscosity of the dope solution significantly. When the PVDF polymer with low melt viscosity was dissolved in the solvent, the obtained dope solution also had low viscosity, which increased the polymer precipitation rate resulting in the formation of membranes with a dense surface layer, long finger-like voids underneath and thus low water flux.

Lin et al. studied the effect of polymer dissolution temperature on the morphological characteristics of microporous PVDF membranes prepared from PVDF/DMF/1-octanol system [51]. It was found that all membranes possessed a symmetric structure composed of a packed bed of nearly equal-sized globules. The globule size was dramatically increased from 0.2 – 0.6 μm to 10 – 50 μm whilst raising the dissolution temperature from 50 $^{\circ}\text{C}$ to 110 $^{\circ}\text{C}$. However, the interconnecting parts did not seem to scale with the size of the globules, which resulted in the significantly decreased membrane mechanical strength. In their study, the authors also

carried out a maturation study, in which the dope solution was sealed and aged at 25 °C for an extended period of time before phase inversion. The study showed that the lower the dissolution temperature, the faster the dope solution gelled. In other words, the metastable state of dope solutions was affected by the dissolution temperature. Although all the dope solutions had the same appearance of a clear fluid, those prepared at lower temperatures might contain some invisible nuclei. Those nuclei would strongly influence the phase separation process when the cast polymer solution was immersed into the coagulation bath. As a result, the final membrane structure could be simply controlled by the dissolution temperature and maturation time of the dope solution without changing any other parameters.

In order to optimize the membrane structure for better performance in the application of specific filtration processes, additives have been employed for various functions, such as changing the phase separation mechanism, increasing or decreasing the polymer precipitation rate, or playing a role of pore forming agents. The additives involved in the preparation of PVDF membranes can be categorized into three types, i.e. low molecular weight additives (e.g. LiCl and LiClO₄), high molecular weight additives or polymeric additives (e.g. poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG)) and other types of additives (e.g. glycerol and water) [24].

LiCl is one of the most commonly used low molecular weight additives and has been extensively studied as a pore forming agent in the preparation of PVDF membranes [52-54]. For example, Bottino et al. investigated the effect of LiCl addition on the formation mechanism and overall properties of PVDF ultrafiltration membranes prepared with DMAc, DMF and NMP as the solvent [52]. The experimental results implied that the addition of LiCl in the dope solution could cause a considerable increase in the dope solution viscosity and prompt the gelation induced by crystallisation. The authors attributed the increase in the dope solution viscosity to the strong interaction between LiCl and the solvent, and between Li⁺ cation and the electron donor group of PVDF. Moreover, the addition of LiCl facilitated the formation of macrovoids in the membrane structure by enhancing the polymer precipitation rate due to the high tendency of LiCl to mix with water and the adverse effect of LiCl on the stability of the dope solution.

PVDF membranes with ethanol, LiClO₄ and PVP (M_w = 10,000) added to the dope solution were prepared using DMAc as the solvent by Yeow et al. [47]. All the three additives were found to move the polymer precipitation curve to the left following the trend of LiClO₄ >

PVP > ethanol > no additive, which means that a least amount of non-solvent would be required to promote the phase separation in the PVDF/DMAc/LiClO₄ system. Besides, the addition of the three additives and other non-solvent additives such as water, glycerol and ethanol, had interesting effects on the phase separation process and the resultant membrane performance [48]. For example, adding LiClO₄ could promote the gelation process induced by PVDF crystallisation, whereas the existence of glycerol was adverse to the gelation process. It was also found that the combined addition of PVP and non-solvent water in the dope solution could enhance the membrane permeability from very low to 1640 litre per square meter membrane area per hour (LMH).

Kong and Li compared the structural and performance characteristics of hollow fibre membranes prepared from PVDF/DMAc/water system with and without PVP addition in the dope solution [54]. Both membranes had an asymmetric structure composed of a dense skin layers with macrovoids underneath and sponge-like layer sandwiched in between. It was found that the PVDF precipitation rate was accelerated due to PVP being hydrophilic and very well miscible with water in the coagulation bath. Consequently, the formation of larger macrovoids and cavities underneath the outer and inner skin layers was observed. In addition, the thicknesses of the sponge-like supporting layer and the overall membrane were decreased and the membrane effective porosity was significantly increased by two orders of magnitudes upon the addition of PVP. In conclusion, the PVP doped membrane had smaller membrane resistance and larger water permeance compared to the neat PVDF membrane. Similar results have been obtained by Deshmukh et al. [55] and Wang et al. [56].

2.2.2.2.3 *Coagulation Bath*

Apart from solvent selection and dope solution control, the coagulation bath also plays an important role in determining the ultimate membrane morphology. As discussed in previous sections, the phase separation in the NIPS process is competition between liquid-liquid demixing and polymer crystallisation. Although crystallisation is thermodynamically favoured, in some cases it may be suppressed by liquid-liquid demixing due to the fast mass transfer between the solvent and the non-solvent. It should be noted that the composition of the coagulation bath affects the kinetic factor and is one of the key elements deciding the sequence of liquid-liquid demixing and crystallisation during the phase separation process.

For example, when PVDF membranes are prepared with DMF as the solvent, the use of a strong non-solvent, such as water, would lead to rapid liquid-liquid demixing occurring

before polymer nucleation. In this case, liquid-liquid demixing would dominate the phase separation process leading to the formation of asymmetric membranes with a dense surface layer and a sublayer comprising of finger-like pores and cellular pores [57, 58]. When a soft non-solvent, such as 1-octanol [57] or a mixture of solvent DMF and non-solvent water [58], is employed, mass transfer of the solvent and non-solvent is so slow that nucleation would take place first forming membranes with uniform microporous structure packed with spherical particles.

Yeow et al. employed three non-solvents including water, ethanol and glycerol in the preparation of PVDF membranes using DMAc as the solvent [47]. It was found that water was the strongest non-solvent while ethanol was the weakest for the PVDF/DMAc/non-solvent system.

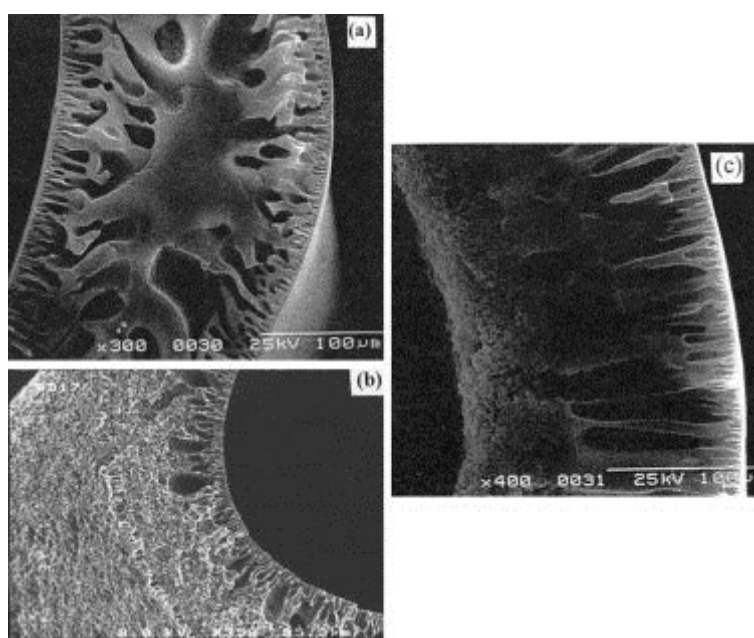


Figure 2.10 SEM images of cross-section of PVDF hollow fibres coagulated in (a) internal: water; external: water; (b) internal: water; external: 50% (vol.) ethanol in water; (c) internal: ethanol; external: water [54]

It should be noted that the phase separation occurring from the top to bottom surfaces in the casting process is different to the phase separation in the spinning process, which takes place from both the internal and external surfaces of the hollow fibre. In this case, two different structures near the outer and inner skin layers may be obtained by altering the composition of the external and internal coagulants. For instance, Kong and Li added ethanol to either the external or the internal coagulant in the PVDF hollow fibre spinning process and studied the effects of ethanol addition on the membrane morphology and filtration performance [54]. As

shown in Figure 2.10, the SEM images of the cross-sectional morphology of the PVDF hollow fibres clearly illustrated the dependence of the skin and macrovoids formation on the corresponding coagulation bath. The skin layer could be completely eliminated due to the slow polymer precipitation rate when a substantial amount of ethanol was involved. However, the results of filtration tests suggested that the removal of the outer skin layer might lead to reduced water flux rather than improved flux. This was probably caused by the formation of the sponge-like structure composed of dead pores near the outer skin of the hollow fibre.

Similarly, Zhu and Zhang prepared PVDF hollow fibre membranes from the PVDF/TEP/water system via the NIPS method [59]. The effects of the bath strength on the membrane formation mechanism and membrane morphology were investigated by blending the water bath with different amounts of TEP. The authors found that solid-liquid demixing was the dominant phase separation mechanism when pure water was used as the non-solvent. By adding TEP to the water bath, solid-liquid demixing was suppressed by delayed liquid-liquid demixing. As a result, the obtained membrane morphology could be changed from an asymmetric structure with a dense skin layer to a completely porous symmetric structure by changing the bath composition from pure water to 40 vol.% TEP.

Apart from the bath composition, the bath temperature is another parameter affecting the phase inversion process. Wang et al. prepared PVDF membranes from the PVDF/DMAc/water system and studied the effects of the coagulation bath temperature on the formation mechanism as well as the morphological and crystal structures of the prepared membranes [60, 61]. It was found that at low temperatures (15 °C and 25 °C), liquid-liquid demixing was delayed and gelation initiated by the formation of PVDF microcrystallites was the dominant membrane formation mechanism. In the gelation process, the PVDF microcrystallites connected various polymer chains together and formed a three-dimensional network in the final membrane. However, when the coagulation bath temperature was increased to 60 °C, the gelation curve shifted closer to the binodal curve. In this case, the gelation process was suppressed by the liquid-liquid demixing caused by solvent and non-solvent exchange and thus obtain membranes with a bicontinuous interconnected structure.

Similar work has been conducted by Fadaei et al., who explained the effect of bath temperature on membrane morphology based on the system equilibrium state [62]. The experimental results suggested that compared to the 25 °C bath temperature, liquid-liquid demixing was favoured with a low polymer precipitation rate at 60 °C bath temperature due to

increased system entropy and thus lower Gibbs free energy. Formation of fewer macrovoids and a columnar structure was detected in the 60 °C membrane with relatively higher membrane shrinkage. Besides, Fourier transform infrared spectroscopy (FTIR) analysis indicated that the elevated bath temperature suppressed the formation of PVDF β form crystallite, which was probably due to the lower thermodynamic stability of β crystallite.

2.2.2.2.4 *Other Factors*

In addition to the three key factors involved in the NIPS process, there are other parameters influencing the phase separation mechanism and the resultant membrane structure, performance and properties.

For example, the effect of evaporation time before immersing the cast polymer film into the water bath was investigated by Munari et al. [63], who prepared PVDF membranes using DMF and NMP as the solvent mixed with acetone and tetrahydrofuran (THF) cosolvents. It was found that when a high-boiling-point solvent (DMF or NMP) was used, the evaporation time seemed to have little influence on the membrane structure and properties. However, when a low-boiling-point solvent (acetone or THF) was present in the system, the membrane structure was affected by the evaporation of the cosolvent before phase inversion. If the evaporation time was long enough, the polymer would precipitate before contacting water in the coagulation bath. In this case, a very brittle membrane would be formed, and it is not applicable in real practice.

Corresponding to the evaporation time in the casting process, in the spinning process, the distance of the air gap in which the spun hollow fibre is exposed to air before being immersed into the coagulation bath is one of the parameters affecting the skin morphology. Khayet prepared PVDF hollow fibre membranes at various air gap ranging from 0 cm to 80 cm and studied the variation in membrane structure and filtration performance [64]. The characterisation results indicated that an elongational stress caused by gravity was applied on the spun hollow fibre by the air gap and such stress would induce molecular orientation and polymer chain package. As the air gap increased, the wall of the hollow fibre became thinner and denser and thus decreasing the membrane permeability but improving the selectivity due to the reduced pore size. In addition, it was found that the elongational stress applied on the external and internal surfaces of the membrane was different. The results showed that the inner skin layer was responsible for separation at a low air gap of less than 20.3 cm, whereas the outer skin layer had smaller pore size at high air gaps.

Despite the air gap, the extrusion rates of the dope solution and the internal coagulant (bore fluid) are two other factors influencing the membrane formation in the spinning process. Generally, the outer diameter and thickness of the hollow fibre membrane increases as the dope solution extrusion rate is increased. On the other hand, when the bore fluid extrusion rate is very low, the lumen of the hollow fibre may not be round in shape. The prepared membrane is not uniform and cannot stand high pressure in real applications. However, if the bore fluid extrusion rate is too high, holes may be created on the hollow fibre during the phase inversion process. In this case, the membrane selectivity is ruined without significant improvement on the membrane permeability.

To sum up, the phase separation mechanism and the membrane morphology, performance, and properties are determined by the combination of all the affecting parameters involved in the NIPS process.

2.2.3 Typical Features of PVDF Membranes

It is well known that the PVDF MF and UF membranes are prepared predominantly by the NIPS technique both in the laboratories and in the industrial manufacturing processes. As discussed in Section 2.2.2.1, the liquid-liquid demixing process is mainly responsible for the membrane structure formed in the NIPS process. Basically, the PVDF membranes normally possess an asymmetric structure consisting of a thin skin layer supported by finger-like voids and/or a sponge-like sublayer. The thin surface layer of PVDF ultrafiltration membranes often has low surface porosity, which is adverse to the water permeation. In most cases, the existence of macrovoids is observed in the cross section of the membrane. In fact, the finger-like voids can be treated as macrovoids with an organized and highly elongated shape [30]. Although macrovoids have porous walls, the porosity is very low, similar to the skin layer. Generally, the presence of macrovoids attenuates the membrane mechanical stability under high pressure and membrane permeability.

Macrovoids are normally formed when instantaneous demixing occurs. The formation mechanisms of macrovoids have been extensively studied and various theories have been proposed in the literature. These theories can be classified into two types: one is growth of the polymer-lean phase close to the interface of the polymer solution and non-solvent; the other is based on the invasion of non-solvent into the polymer solution. In the former type of theories, the formation of macrovoids starts from the nucleation of the polymer-lean phase upon liquid-liquid demixing and grows further by diffusion of the solvent from the surrounding polymer

solution until the polymer precipitates when the polymer concentration is too high at the interface [65]. However, in the latter type of theories, the mechanism behind the invasion of non-solvent can be interpreted as interfacial instabilities. The instability of the surface disturbance may be attributed to different sources, such as interfacial tension difference [66], viscosity difference [67] or density difference [68-70]. The exact mechanism of macrovoid formation still remains arguable.

On the other hand, the sponge-like structure is of a cellular texture, and the pores may be open or closed. The formation mechanism of the cellular structure could be explained based on the nucleation and growth of the droplets of the polymer-lean phase in the polymer-rich phase [25, 71]. If the droplets of the polymer-lean phase grow large enough to coalesce before the surrounding polymer-rich phase solidifies, membranes with an open porous structure and thus high water permeation will be formed, which is favoured for MF and UF membranes. If not, a cellular structure composed of closed pores will be obtained and such a structure increases the trans-membrane resistance dramatically.

Apart from the above-mentioned structural drawbacks in the PVDF membranes prepared via the NIPS method, there are other problems limiting the further developments and applications of PVDF membranes. For example, low permeation flux and membrane fouling caused by the hydrophobic nature of PVDF material are two issues that PVDF membranes have always suffered from when applied in the MF and UF processes. Most commercial PVDF membranes for industrial use only allow pure water to permeate with flux of less than 200 LMH under 1 bar pressure difference across the membrane. To compensate the low flux of PVDF membranes, larger membrane areas are required to treat a large volume of water. The requirement of large membrane area increases not only the capital investment but also the daily operating costs (for energy and maintenance) of the filtration units.

Meanwhile, susceptibility to fouling is the major drawback of PVDF membranes in the application of water/wastewater treatment, especially for wastewater containing organic compounds such as oil and proteins. The adsorption and accumulation of organic compounds on the membrane surface and into the pore channels will result in severe reduction in the permeate flux. Hashino and co-workers have conducted an investigation on the effect of three different common polymeric membrane materials on membrane fouling using bovine serum albumin (BSA) as a model protein [72]. The authors found that compared to poly(ethylene-co-vinyl alcohol) (EVOH), polyether sulfone (PES) membranes, PVDF membranes exhibited the

highest amount of BSA adsorption and the most rigid BSA adsorption layer in the static protein adsorption experiment. Moreover, the PVDF membranes showed drastic flux decline in the dynamic filtration test with the protein solution. The authors attributed the severe fouling to the strong physicochemical interactions between PVDF and BSA detected by the adhesion force measurements. In real practice, frequent backwashing and chemical cleaning are required to remove the fouling layer. Thus the lifetime of the membranes is decreased and the operation costs are increased.

2.3 Modification of PVDF Membranes

PVDF MF/UF membranes have been extensively studied, successfully commercialized and widely applied in water/wastewater treatments for decades in spite of their structural and material's intrinsic drawbacks. In order to enhance the membrane permeability and fouling resistance, various techniques have been developed to improve the hydrophilicity of PVDF membranes. According to Liu et al. [24], the various hydrophilic modification techniques could be classified into two categories, i.e. surface modification including surface coating, surface grafting, and blending modification using hydrophilic polymers, amphiphilic copolymers and inorganic nanoparticles as the functional additives. The recent progress in the hydrophilic modification of PVDF membranes will be reviewed in this section.

2.3.1 Surface Modification

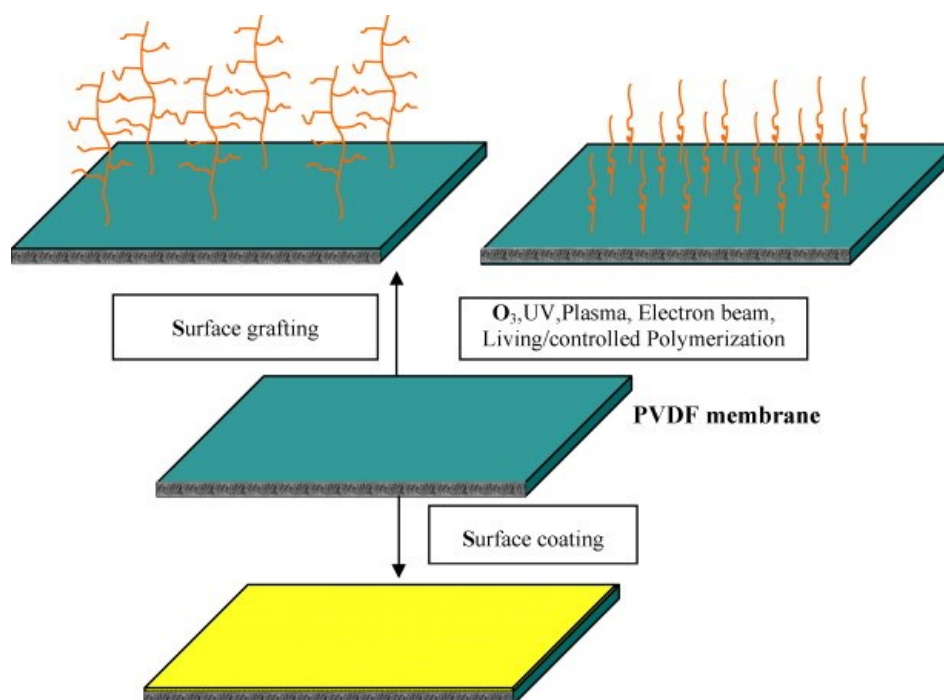


Figure 2.11 Schematic of surface modification of PVDF membranes [24]

Figure 2.11 shows the schematic of surface coating and surface grafting of PVDF membranes in the hydrophilic modification process [24]. It can be seen that surface coating is conducted by simply depositing a thin hydrophilic layer on the membrane surface. However, in the surface grafting process, the hydrophilic layer is formed by bonding functional chains to the membrane surface via high-energy treatment or living/controlled polymerisation. Each method has its own advantages and disadvantages.

2.3.1.1 Surface Coating

As introduced above, surface coating is the simplest way to improve membrane surface hydrophilicity. It is conducted by coating or depositing a functional hydrophilic layer on the hydrophobic membrane surface via physical adsorption, cross-linking or sulfonation. A major drawback of this technique is that the surface layer can be easily washed away during operation, especially when the pH of the solution changes. Furthermore, the membrane resistance may be increased due to the undesirable accumulation of the coating molecules in the pores, which leads to a reduction in water flux even though the membrane hydrophilicity is improved.

Hydrophilic fouling-resistant poly(vinyl alcohol) (PVA)-based polymer PVA-OCH₂COONa was synthesised by Jang et al. and was subsequently employed to modify PVDF membranes by a simple dip-coating method [73]. The characterisation results implied that the PVA coated membranes had a reduced pore size, improved surface hydrophilicity and decreased surface roughness. In addition, the modified PVDF membrane was endowed with excellent anti-fouling property due to the high hydrophilicity and electronegativity of the sodium carboxymethyl groups in the coating layer. It showed enhanced water permeability and slower flux decline in the fouling test.

In the work conducted by Li et al., a thick sulfobetaine polymer UF sieving layer was formed by graft polymerisation of sulfobetaine with PVP, and was then cross-linked with the PVDF hollow fibre MF membranes [74]. It was found that the thickness and selectivity of the formed sulfobetaine sieving layer could be controlled by varying the composition of the swelling solution without compromising membrane permeability. The optimal performance was achieved after immersing the prepared membrane in 20 mmol/L NaCl solution at 60 °C and the treated membrane showed pure water flux of 590 LMH with molecular weight cut-off (MWCO) of 95 – 110 kDa in the filtration test. Immersion of the membrane in water would result in loss of the membrane selectivity and protein separation efficiency, which could be restored after swelling the membrane in the NaCl solution again.

Hyper-brush PEGylated block copolymers polystyrene-*b*-poly(ethylene glycol) methacrylate (PS-*b*-PEGMA) with varied PS/PEGMA ratio were synthesised via ATRP by Lin et al. [75]. They were then coated onto PVDF MF membrane surface by hydrophobic-driven anchoring based on the van der Waals force between the styrene groups in the copolymer and the fluorine atoms on membrane surface. A self-assembled monolayer of the copolymer was formed on the membrane surface without aggregation, which means that the original pore structure of the membrane would be maintained. It was found that the membrane surface hydrophilicity and fouling resistance were strongly affected by the surface coverage and chain conformation of the hydrophilic PEGMA brushes on the membrane. As shown in Figure 2.12, excessive increase in the molecular weight of the PEGMA block might lead to reduced adsorption of the copolymer on the membrane surface due to the increased steric hindrance of the hyper-brush PEGylated side groups. The filtration tests indicated that the optimum antifouling performance in terms of superior resistance to proteins (BSA and lysozyme) and bacteria (*E. coli* and *S. epidermidis*) could be achieved over 12 days when the PS/PEGMA ratio was between 1.5 and 2.0 with copolymer molecular weights above 20.0 kDa.

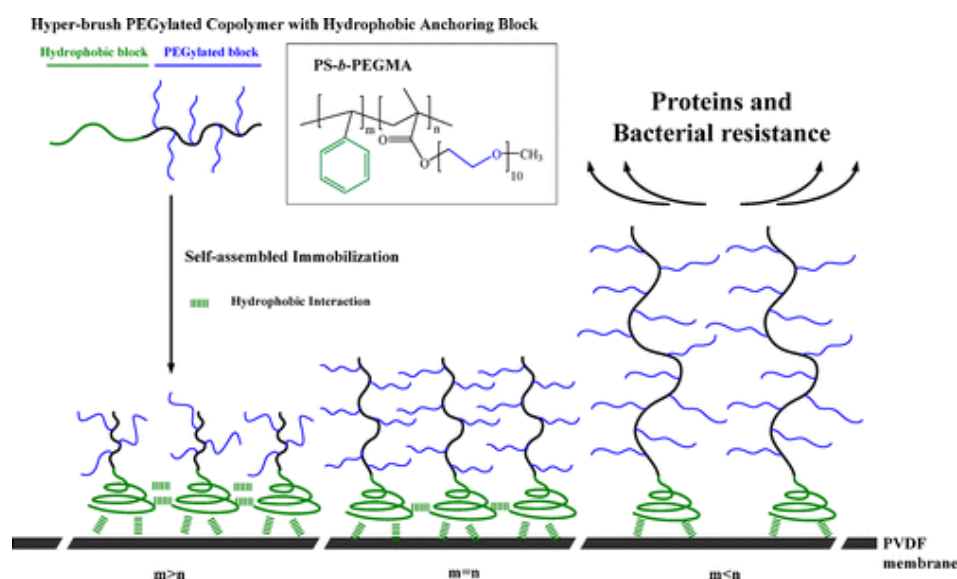


Figure 2.12 Hydrophobic-driven anchoring of PS-*b*-PEGMA copolymers on PVDF membrane surfaces with various PS/PEGMA ratios [75]

2.3.1.2 Surface Grafting

The instability problem of the coating layer in the surface coating method can be solved using the surface grafting method, in which the hydrophilic layer is chemically bonded to the membrane surface by high-energy treatment or living/controlled polymerisation. The high-energy treatment includes UV [76], plasma [77], and electron beam [78], whereas

living/controlled free-radical polymerisation [79-81] are mainly atom transfer radical polymerisation (ATRP) [82, 83] and reversible addition-fragmentation chain-transfer (RAFT) polymerisation [84]. In particular, it is possible to prepare well-defined polymers with desirable structures on the membrane surface via the latter technique. However, surface grafting is always restricted on the top and/or bottom of the membrane, whereas the pore channels remains unchanged due to the limited diffusion of the modifying agents into the membrane pores. In addition, the involvement of the high-energy treatment makes it expensive and difficult to scale up, while the polymer chains may block the membrane pores leading to flux decline.

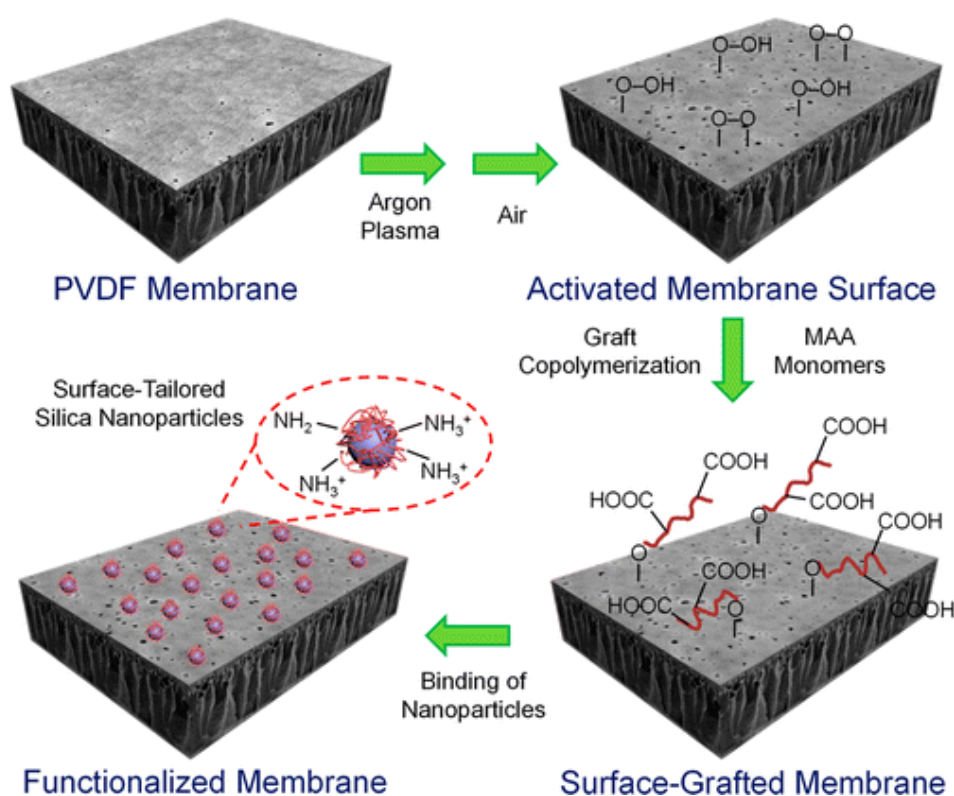


Figure 2.13 Schematic protocol of PVDF membrane functionalization including plasma treatment, graft copolymerization and nanoparticle binding [85]

Liang and co-workers prepared highly hydrophilic PVDF UF membranes by grafting superhydrophilic silica nanoparticles onto the membrane surface [85]. As shown in Figure 2.13, the hydrophobic PVDF membrane was pre-treated by plasma induced graft copolymerization with poly(methacrylic acid) (PMAA) in order to generate carboxyl groups on the membrane surface serving as anchor sites. The silica nanoparticles were surface-tailored with amine-terminated cationic ligands, and were then irreversibly bounded to the PMAA modified membrane surface via a simple dip-coating process. The experimental results demonstrated that the membrane surface property was successfully converted from hydrophobic to

hydrophilic after functionalization. The results also proved that the tightly bound hydration layer on the membrane surface prevented the adhesion of foulants on the membrane surface, which effectively improved the membrane fouling resistance. In their following work [86], the antifouling performance of the surface modified membrane was investigated using sodium alginate (SA), BSA and Suwannee River natural organic matter (NOM) as model organic foulants. The results indicated that the superhydrophilic PVDF UF membrane possessed excellent fouling resistance, which coincided with the reduction of foulant-membrane adhesion forces. It was also found that the membrane selectivity in terms of MWCO was not adversely affected by surface functionalization of the membrane.

In Li and co-workers' work, PVDF hollow fibre membranes with a hydrophilic and anti-fouling surface layer was prepared by ATRP of 2-hydroxyethyl methacrylate (HEMA) followed by Ce (IV)-graft copolymerization of zwitterionic 3-(methacryloylamino) propyl-dimethyl-(3-sulfopropyl) ammonium hydroxide (MPDSAH) [87]. The high-density grafting of polyMPDSAH on the PVDF membrane surface via polyHEMA chains as initiation sites was confirmed by FTIR, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). As the grafting amount increased, the membrane fouling resistance was significantly enhanced in terms of improved surface hydrophilicity and decreased amount of protein adsorption. In the filtration test, the modified membrane adsorbed less protein fouling, and most of which was reversible. Moreover, the mechanical properties of the PVDF membrane were improved due to the existence of the zwitterionic surface layer.

2.3.2 Blending Modification

Compared with surface modification, blending modification has attracted enormous amounts of studies because of its simplicity and easy scale-up. In the blending modification process, additives with desirable properties are mixed in the dope solution, followed by phase inversion forming modified membranes. This means that the preparation and modification of PVDF membranes are combined in a single-step process without pre- and/or post-treatment steps, which are usually involved in surface modification. Furthermore, there is no limitation either on the modified sites or on the membrane configurations. The additives utilised in blending modification of PVDF membranes can be grouped into three types, i.e. hydrophilic polymers, amphiphilic copolymers, and inorganic nanoparticles.

2.3.2.1 Hydrophilic Polymers

Hydrophilic polymers, such as PVP and PEG, are normally employed as pore forming agents. They may be washed away during the coagulation process and/or operation process due to their good solubility in water.

Rajabzadeh et al. investigated the effects of blending additives including PVP and poly(methyl methacrylate) (PMMA) on the modified PVDF hollow fibre membranes prepared via the TIPS method [44]. It was found that adding PMMA had little influence on the morphology and properties. However, the introduction of PVP to the PVDF/solvent system led to the formation of a dense skin layer, and suppressed the growth of PVDF spherulites because of the low compatibility between PVDF and PVP. In addition, the membrane hydrophilicity, fouling resistance, maximum stress and elongation ratio were all improved by the addition of PVP.

Lang and co-workers prepared PVDF hollow fibre membranes using NMP as the solvent and PVP with four different molecular weights as the additive [88]. It was found that instantaneous demixing occurred in all cases leading to the formation of PVDF hollow fibres with a similar asymmetric structure. All the fabricated PVDF membranes had a nodular outer skin layer and a porous inner skin layer with finger-like voids underneath both skin layers, and sponge-like structure sandwiched in between. By increasing the molecular weight of PVP, the polymer precipitation rate decreased due to the increased dope viscosity. Moreover, a thicker but less porous inner skin layer was formed and more PVP was retained in the membrane matrix after the phase inversion process. Thus, both permeability and rejection of the membrane were affected by the PVP addition. In their work, the maximum pure water flux reached 316.7 LMH bar⁻¹ with BSA rejection of 65.6% when the molecular weight of PVP was 24,000.

Fadaei et al. produced PVDF flat sheet membranes from PVDF/DMAc/water system with PEG as the hydrophilic additive [62]. All membranes exhibited an asymmetric structure composed of a thin dense surface layer with finger-like voids underneath and a sponge-like cellular supporting layer. The addition of PEG favoured the formation of more regular finger-like voids and macrovoids in the membrane, which contributed to the enhanced membrane porosity and water permeation. In addition, the FTIR analysis suggested that the presence of PEG in the system promoted the formation of hydrogen bond with PVDF. It in turn interfered with the PVDF/DMAc interactions and facilitated the formation of collapsed PVDF chains, i.e. α form crystalline.

L2MM, a hydrophilic polyurethane additive with hydroxyl end-groups from PEG involved in the synthesis process, was employed by Pezeshk and Narbaitz in the preparation of modified PVDF membranes [89]. It was found that the L2MM blended PVDF membranes possessed lower water contact angle compared to the pure PVDF membrane sample. In the filtration test with Ottawa River Water, the modified membranes showed better filtration performance in terms of a 144% higher flux compared to the pure PVDF membrane. However, the flux decline during filtration was 4% higher and the total organic carbon (TOC) removal was 3% lower than those of the unmodified membrane. Nevertheless, compared to a more hydrophilic commercial PVDF membrane, the L2MM modified membrane still displayed smaller flux decline, slightly higher final flux at steady state, higher cumulative permeate production and higher TOC removal. Furthermore, simulations of the filtration process indicated that both cake formation on the membrane surface and blockage inside the membrane pores were important fouling mechanisms.

Zhang and co-workers studied the preparation and characterisation of PVDF/PES blend membranes with PVA addition [90]. Although the membrane morphology was nearly unaffected by the PVA addition, the modified membranes exhibited higher porosity, lower contact angle and larger pure water flux compared to the pristine membrane. In the fouling analysis, they also showed higher critical flux and decreased fouling rate. Furthermore, the extended Derjaguin-Landau-Verwey-Overbeek theory was employed to evaluate the membrane antifouling performance. It suggested that the PVA addition improved the cohesion free energy of the membrane and the energy barrier between foulants and membrane surface. Both suppressed the adsorption of foulants on the membrane surface and thus increasing the membrane fouling resistance.

Apart from the low-molecular-weight hydrophilic polymers, cellulose acetate (CA) with high molecular weight has also been used as an additive to prepare PVDF/CA blend membranes through the NIPS technique [91]. It was found that as the CA/PVDF ratio increased, the membrane hydrophilicity, pore size and porosity were increased, resulting in improved pure water flux and reduced reversible fouling. The highest pure water flux of 522 LMH and lowest total fouling ratio was achieved when the CA/PVDF ratio of the membrane reached 20%. Further increase of the CA amount turned out to decrease the membrane porosity and pure water flux. This could be attributed to the formation of denser parts and fewer macrovoids in the membrane due to the low miscibility of CA and water. The blending of CA also had adverse effects on the membrane performance and mechanical strength. For example, the increased

pore size due to CA blending might lead to the BSA diffusion into the pore channels and further aggravate the membrane fouling. Moreover, decomposition of CA was observed when the blend membrane with 30% CA was applied in sewage wastewater filtration with chemical cleaning involved.

Bioinspired polydopamine (PDA) nanoparticles were synthesized in different reaction mediums by Jiang et al. and were then used as a pore forming agent and hydrophilic additive to prepare PVDF/PDA blend membranes [92]. It was found that the prepared membranes possessed good stability, and enhanced membrane hydrophilicity, water permeability and fouling resistance. In particular, blend membranes with uniform surface pores and an interconnected porous structure could be obtained through in situ synthesis of PDA. They possessed the highest water flux and tensile strength among the three different membranes.

2.3.2.2 Amphiphilic Copolymers

First studied by Mayes et al. [93], blending hydrophobic PVDF with an amphiphilic copolymer has been reported to successfully improve the desirable properties of the prepared membranes. During the phase separation process, the hydrophobic side chains of the amphiphilic copolymer, such as PVDF itself or PMMA, are compatible with PVDF bulk material to promise stability. While the hydrophilic side chains, such as PEG and its derivatives [94-96], are substantially enriched on the membrane and water interface, including the membrane surface and pore channels. Thus, spontaneous wettability, enhanced fouling resistance and water flux can all be achieved.

A graft amphiphilic copolymer PVDF-g- poly(oxyethylene methacrylate) (POEM) was synthesised by ATRP method and was then used as an additive to prepare PVDF hollow fibre membranes by Abed et al. [97]. In the conventional ATRP synthesis process of the copolymer, a mixture of methanol/petroleum ether is normally used to wash and purify the product and is highly volatile, toxic and expensive [93]. In this work, the researchers optimised the synthesis approach by using water instead. The developed process involved fewer steps and was more environmentally friendly compared to the conventional method. By adding 5 wt.% of the copolymer, the water contact angle on the membrane surface was decreased from 90.1° to 65.6° , and the pure water flux increased from 0.3 LMH bar^{-1} to $130.5 \text{ LMH bar}^{-1}$. The results revealed significant improvement on both the hydrophilicity and fouling resistance of the membrane by blending the copolymer. However, SEM observation of the membrane structure illustrated the formation of macrovoids, which was probably due to the rapid phase separation caused by the

affinity of the hydrophilic POEM side chains for water. Moreover, the presence of macrovoids decreased the mechanical strength of the fibre by about 50%. This limited the wide-range applications of such modified PVDF membrane and was regarded as the major drawback of PVDF membrane blending modification with amphiphilic copolymers.

Chen and co-workers produced PVDF membranes with an amphiphilic copolymer PVDF-g-PEGMA as the additive via the NIPS method [98]. As shown in Figure 2.14, the flat sheet membranes prepared with NMP as the solvent displayed unique pillar-like surface morphology. They also demonstrated a high pure water flux of 2173 LMH bar⁻¹ with a good SA rejection ratio of 89% in the filtration test. Based on a series of characterisations, the formation of such pillar-like structure could be explained as follows. In the phase inversion process, the PVDF side chains in the copolymer mixed with the PVDF in the matrix, whereas the PEGMA side chains self-enriched on the surface. Compared to other solvents, the use of NMP allowed the PEGMA side chains to have enough time to transfer onto the membrane surface and then repel each other, forming the unique pillar-like structure.

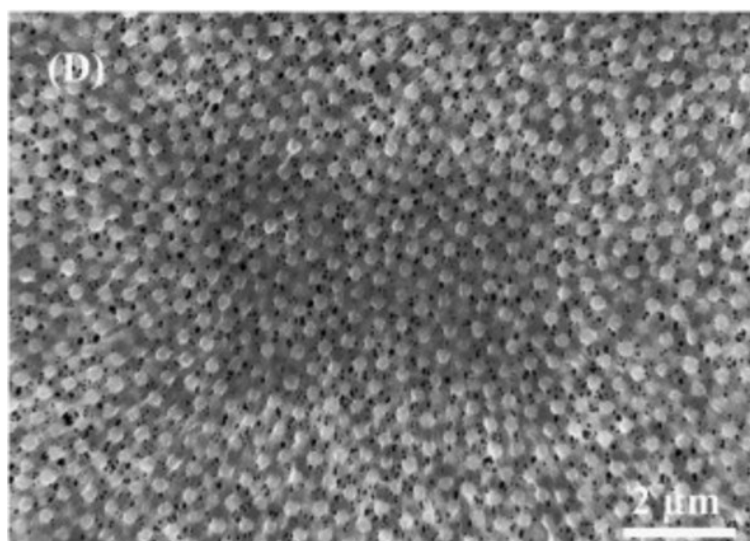


Figure 2.14 SEM image of the top surface structure of PVDF membranes prepared using NMP as the solvent and PVDF-g-PEGMA as the additive [98]

Apart from PEG and its derivatives, other polymers such as hydrophilic PVP [99], biocompatible poly(*N,N*-dimethylacrylamide) (PDMAA) [100], zwitterionic poly(*N,N*-dimethylamino-2-ethylmethacrylate) [101], and nontoxic and nonantigenic polyacryloylmorpholine [102] have been grafted onto PVDF backbones. The synthesised copolymers were then adopted as additives or membrane materials in the preparation of hydrophilic modified PVDF membranes with anti-fouling property. For example, PVDF-g-

PDMAA copolymer was prepared by Yang et al. via pre-irradiation induced graft copolymerisation and was then made into MF membranes through the NIPS method [100]. Compared to the pristine PVDF membranes, the PVDF-g-PDMAA MF membranes had improved surface hydrophilicity and decreased pore size. Thus, they showed reduced water flux but anti-fouling performance in the filtration test. The superior anti-fouling property of the modified membrane was attributed to the enhanced surface hydrophilicity, which prevented the protein adsorption. In addition, it was found that a commercial PVDF membrane with similar pore size and higher hydrophilicity showed lower fouling resistance to the proteins than the PVDF-g-PDMAA membrane.

In addition to hydrophilicity, amphiphilic PVDF copolymers with other functional side chains have been employed to endow PVDF MF/UF membranes with stimulus-sensitive properties, such as pH-sensitivity [103-105], temperature-sensitivity [106-108] and redox-sensitivity [109], etc.

As known to all, membranes applied in the treatment of water containing organic compounds need to be hydrophilic, which contributes to high water permeability. It is also found that an ideal membrane should be oleophobic, which reduces the adhesion rate of the foulants onto the membrane surface and the interaction strength in between. Consequently, the development of hydrophilic and oleophobic copolymers and their use in the preparation of modified membranes have attracted increasing attention from researchers [110, 111] and industrial manufacturers [112].

For example, poly(acrylic acid)-graft-PVDF (PAA-g-PVDF) was adopted by Zhang et al. as the membrane material to prepare superhydrophilic and underwater superoleophobic membranes for effective separation of oil-in-water emulsions [113]. In the preparation process, the water coagulation bath contained high concentrations of NaCl, which behaved as nuclei in the phase inversion process of PAA-g-PVDF. The resultant membrane surface therefore exhibited a micro/nanoscale hierarchical structure formed by the self-assembly of PAA-g-PVDF micelles, as shown in Figure 2.15. In addition, the prepared membranes had a typical asymmetric structure with finger-like channels throughout the cross section. The specific surface morphology endowed the membrane with several outstanding properties: (1) superhydrophilicity, i.e. the membrane was superwetting with water contact angle of ca. 0°; (2) underwater superoleophobicity in terms of underwater oil contact angle of ca. 160°; (3) high permeability, which was two orders of magnitude higher than commercial membranes under

small operating pressure of less than 0.3 bar or under gravity; (4) high separation efficiency of more than 99.99 wt.%; (5) and anti-fouling properties with no obvious flux decline after 30h filtration of hexane/water emulsion, and full recovery of initial flux after washing the membrane with water in each cycle. All these excellent properties make the prepared membranes a promising candidate for being applied in the treatments of industrial and domestic wastewater.

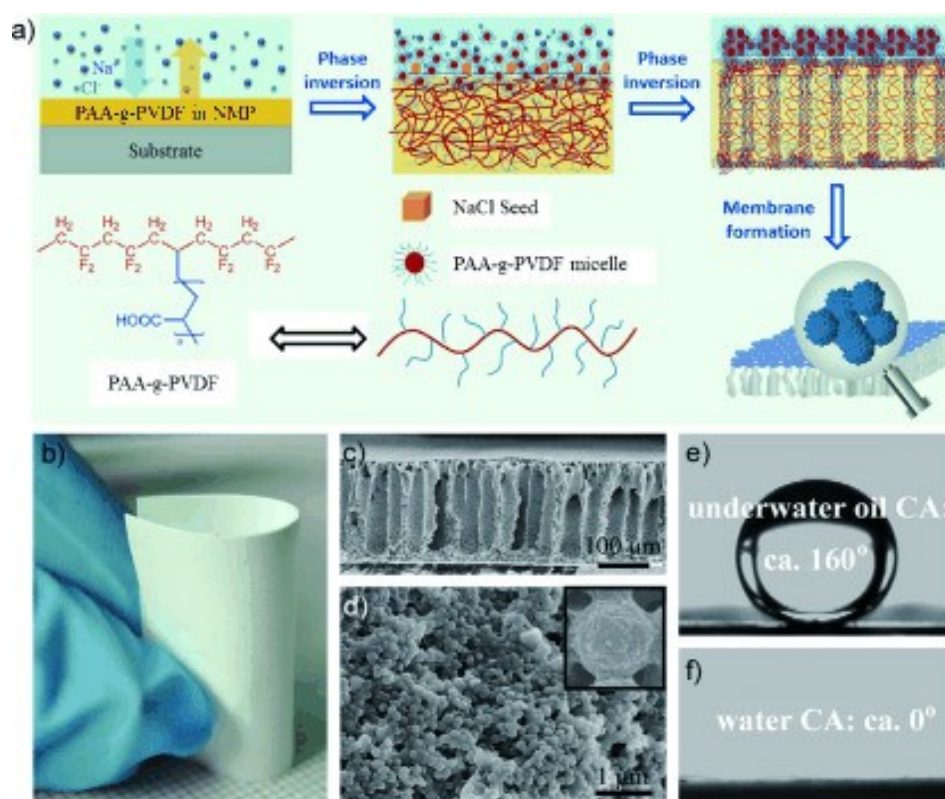


Figure 2.15 a) Schematic of the membrane formation process; b) Photo of the prepared membrane; SEM images of the membrane c) cross section and d) top surface; Photos of e) an underwater oil droplet and f) a water droplet on the membrane [113]

2.3.2.3 Inorganic Nanoparticles

Inorganic nanoparticles have been widely used to modify polymeric membranes for better control of the membrane structure and improving the membrane performance due to two main reasons. One is the remarkable physical and chemical properties of the inorganic nanoparticles. The other is the simplicity of the blending process. Furthermore, blending inorganic nanoparticles can improve the membrane mechanical strength. This is one of its most attractive advantages compared with surface modification and blending modification with hydrophilic polymers or amphiphilic copolymers. The inorganic nanoparticle normally coupled in polymer membranes can be classified into four groups based on dimensions. They are

hydrophilic 0D nanoparticles including metal oxides and metals, 1D nanotubes or nanowires, exfoliated 2D silicate clays and porous 3D zeolites [114]. Nanoparticles that are always used in the blending modification of PVDF membranes include TiO_2 [115-117], SiO_2 [118], Al_2O_3 [119], ZrO_2 [120], ZnO [121], graphene oxide (GO) [122-124], carbon nanotube (CNT) [125], etc. Basically, the homogeneous distribution of nanoparticles in the membrane matrix or on the membrane surface is of great importance in preparing organic-inorganic composite membranes.

Yuliwati and Ismail employed TiO_2 with varied loading amounts and a fixed amount of $\text{LiCl}\cdot\text{H}_2\text{O}$ as the pore-forming hydrophilic additives to prepare porous asymmetric PVDF hollow fibre UF membranes [50]. The TiO_2 nanoparticles possessed high specific areas and good hydrophilicity. They also showed different effects on the phase separation process at different loading amounts. At low TiO_2 loadings, the prepared membranes had finger-like voids extending from both sides with a thin sponge-like sublayer sandwiched in between. They had a small pore size, large porosity and small contact angle. As the addition of TiO_2 increased, the dope viscosity was dramatically increased leading to delayed liquid-liquid demixing and thus suppression of the finger-like void formation. It was also found that the agglomeration of nanoparticles was inevitable at high concentrations resulting in blocked pores and reduced pore size. Consequently, the performance of the modified PVDF membranes in the filtration test of refinery produced wastewater was first enhanced at low TiO_2 loadings and then decreased at high TiO_2 concentrations. The maximum flux of 82.50 LMH and rejection of 98.83% of the refinery wastewater were achieved by PVDF membranes prepared with the addition of 1.95 wt.% TiO_2 .

Targeting at purifying the arsenic contaminated groundwater, PVDF/ ZrO_2 blend flat sheet membranes were prepared via the phase inversion technique by Zheng et al. [126]. The characterisation results indicated that the introduction of zirconia into the membrane matrix enhanced the membrane surface hydrophilicity, surface porosity and thus the water permeability. Meanwhile, the overall membrane porosity was nearly unaffected. In addition, the blend membranes could remove arsenate effectively in the static adsorption test with the solution pH ranging from 3.0 to 8.0. In particular, a maximum adsorption capacity of 21.5 mg/g was achieved by the membrane prepared with the ZrO_2 to PVDF weight ratio of 2:1. This value is even comparable to other adsorbents. It was also found that the blend membranes had high selectivity of arsenate over other anionic ions such as fluoride. Apart from arsenate, more than 99% of *E. coli* was successfully rejected by the zirconia blended membrane in the dynamic filtration test.

Liang et al. modified PVDF membrane by blending a moderate amount of ZnO nanoparticles in the dope solution prior to the phase inversion process [127]. The SEM images and energy dispersive X-ray (EDX) analysis confirmed the enrichment of ZnO nanoparticles on the membrane surface as well as on the wall of the pore channels. The filtration tests revealed that the membrane permeability was almost doubled upon the addition of ZnO by 6.7% of the PVDF weight. Furthermore, the high permeability of the modified membrane could be almost 100% recovered after physical cleaning. On the other hand, the unmodified membrane only achieved 78% flux recovery. The authors attributed the excellent anti-fouling property to the increased membrane hydrophilicity caused by the implantation of ZnO nanoparticles. It was also found that blending ZnO nanoparticles could enhance the membrane mechanical strength.

Zhao et al. developed the preparation of PVDF membranes by blending functionalized multiwall carbon nanotubes (MWCNTs) in the dope solution [128]. In order to avoid agglomeration, the MWCNTs were first surface functionalized by grafting with poly(amine-ester) hyperbranches. The transmission electron microscopy (TEM) and XPS analysis confirmed the stable dispersion of the functionalized MWCNTs at individual nanotube level in the membrane matrix and on the membrane surface. Other characterisations indicated that by adding the functionalized MWCNTs, the membrane hydrophilicity was improved with lower water contact angle. The membrane fouling resistance was also enhanced in terms of less protein adsorbed during the filtration process, and increased flux recovery ratio from 78.4% to 95.7% after the hydraulic cleaning and chemical cleaning processes.

In Xu, Qian and co-workers' research, blending the dope solution with 2D GO and 1D oxidized MWCNTs has displayed extraordinary synergetic effect on the PVDF membrane permeability and fouling resistance [129, 130]. The researchers reported that the dispersion of the mixture of GO and oxidized MWCNTs was better than either component appearing individually. This was probably caused by the bridging effect of oxidized MWCNTs between GO flakes. The experimental results showed that the addition of the two inorganic fillers dramatically increased the membrane surface porosity, hydrophilicity and thus the water permeability. The best performance was achieved when the GO/oxidized MWCNTs ratio was 5:5. In this case, the membrane water flux was improved by 251.73% compared to 85.68% with GO added only and 103.54% with OMWCNTs. Furthermore, this membrane demonstrated high flux recovery of 98.28% in the filtration test, which confirmed the benefit of the synergetic effect of GO and oxidized MWCNTs on the anti-fouling performance of the

membrane. In their following work, the authors adopted GO and organosilane-functionalised GO to prepare modified PVDF UF membranes [131]. Compared to the neat PVDF membrane and GO modified PVDF membrane, the functionalized GO modified PVDF membrane was found to possess better hydrophilicity, larger flux, higher rejection rate and smaller adhesion force with protein foulants. All these performance characteristics proved the enhanced anti-fouling property endowed by the addition of functionalised GO. Moreover, the tensile strength and elongation ratio at the breaking point of the modified membrane were improved by 69.01% and 48.38%, respectively. Such enhancement of the membrane mechanical properties was attributed to the good interfacial interaction between the functionalized GO sheets and the PVDF matrix.

A novel hydrophilic nanocomposite additive, PVP-g-montmorillonite (MMT), was synthesized by *N*-vinylpyrrolidone-grafted polymerisation modification of MMT by Wang et al. [132]. The obtained material was then used to prepare PVDF/PVP-g-MMT nanocomposite UF membranes via the NIPS method. The prepared nanocomposite membranes had a similar asymmetric structure to the neat PVDF membrane. They were all composed of a thin skin layer with finger-like voids beneath and a sponge-like supporting layer. The multi-functional PVP-g-MMT had three main functions in the preparation of the modified PVDF membranes. They are: (1) self-dispersing to ensure good dispersion in the membrane matrix; (2) pore forming to enlarge the size of the finger-like structure and improve the surface porosity; (3) hydrophilic modifying to enhance the membrane surface hydrophilicity. It was also found that the membrane pure water flux was increased from about 15 LMH bar⁻¹ to 74.64 LMH bar⁻¹ with the BSA rejection remaining at an acceptable level of more than 81.1%.

Apart from improved hydrophilicity and enhanced mechanical strength, blending with nanoparticles could endow PVDF membranes with other advantageous properties. For instance, PVDF membranes could gain antibacterial property by immobilization of Ag-based biocides [133, 134]. Membranes with TiO₂ nanoparticles under UV irradiation would show the photocatalytic effect and superhydrophilic effect, which can degrade organic compounds and improve surface hydrophilicity [135].

2.4 Freeze-Drying Method

The recent progress in the preparation and modification of PVDF MF/UF membranes have been reviewed in the previous sections. Generally, PVDF membranes fabricated by the phase inversion technique always have an asymmetric structure composed of a dense skin layer

with finger-like voids underneath and a sponge-like supporting layer. The dense skin layer behaves as a separation barrier and normally possesses low porosity, which together with the hydrophobic nature of the polymer material leads to low membrane permeability. Meanwhile, the presence of finger-like voids becomes weak points reducing the membrane mechanical stability when applied in high-pressure filtration processes. Numerous research works have been conducted on the development of the membrane structure and hydrophilicity as well as other useful properties. However, it has been found that all the modification techniques include either extra chemicals or pre-/post-treatment. Thus, the production cost of the PVDF membranes is increased, which is unfavourable. Consequently, some researchers have placed their attention on the development of the membrane fabrication process by controlling the preparation conditions.

In the NIPS process, complex physical-chemical factors are involved, such as inter-diffusion of solvent and non-solvent, rheology of polymer solution, hydrodynamic interfacial instabilities, and even the ambient temperature and humidity [24, 29, 136]. As a result, controlling the quality of final membrane products is extremely complicated, and often an ideal structure with minimised permeation resistance is difficult to achieve. On the other hand, a few investigations have been carried out to study the effect of temperature on the PVDF membrane morphology prepared via the TIPS method, particularly using DMSO as the solvent. According to Bottino's work, the membranes prepared with DMSO by the NIPS technique had large-size cavities without a defined shape grown across the membrane structure. This means that using DMSO is adverse to the control of cavity formation in the NIPS process [46]. Nevertheless, DMSO is a green solvent, which is environmentally friendly. Furthermore, it has a well-known melting point of 18.5 °C, which means that the crystallization of DMSO may affect the phase inversion of PVDF in the TIPS process at lower temperatures.

For example, Su et al. developed a freeze-gelation method based on the TIPS technique. In their work, the PVDF films cast with various dope concentrations were placed in a refrigerator at -10 °C for 2 h before being immersed in water for solvent exchange [137]. As shown in Figure 2.16, the membranes were composed of tightly accumulated PVDF spherulites. The authors claimed that the crackles (20 wt.% and 30 wt.% PVDF in the dope solution) and pores (40 wt.%) on the membrane surfaces were originally occupied by the solidified DMSO in the frozen casting solution. Such membranes exhibited high water flux in the filtration test and excellent mechanical properties in the tensile test.

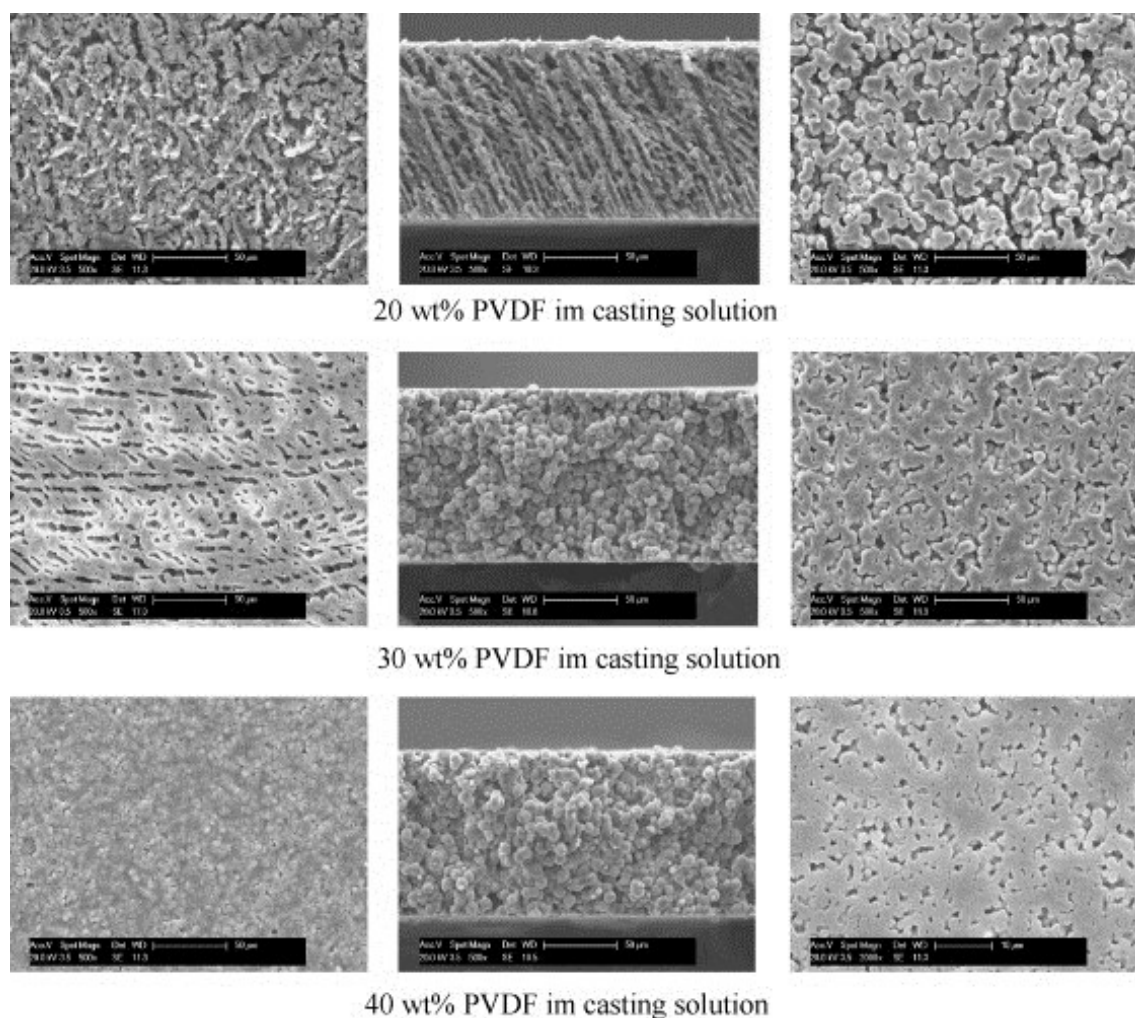


Figure 2.16 SEM images of the top surface (left), cross section (middle) and bottom surface (right) morphologies of PVDF membranes prepared by freeze-gelation method [137]

On the other hand, Kim and Lee prepared PVDF membranes with pores of low tortuosity and high porosity by directional crystallization of DMSO [138]. In their method, the PVDF film cast on a silicon wafer was moved towards liquid nitrogen at a speed of 200 $\mu\text{m/s}$. Directional crystallisation of DMSO was achieved under the temperature gradient provided by the controlled movement of the PVDF film towards the cold source. In the moving process, DMSO molecules are directionally crystallised to form columnar crystallites perpendicular to the membrane surface. After removing the solvent crystallites, pores of low tortuosity and high porosity (80 – 90%) were formed in the obtained membrane. According to the authors' work, the pore size could be effectively controlled within a range from several tens of micrometres to a few hundred nanometres by mixing DMSO with dioxane as the solvent.

Indeed, the techniques employed in the two attempts discussed above are similar to the “freeze-drying” method in the field of materials engineering [139-141]. Apart from phase

inversion, freeze drying is another technique widely used in the preparation of porous materials, and is normally adopted in tissue engineering [142], biological applications [143] and pharmaceutical industries [144]. As reviewed by Qian and Zhang [145], a wide range of porous and micro-/nano-structured materials could be prepared from solutions, emulsions or colloidal suspensions via the controlled freezing and freeze-drying method.

2.4.1 Mechanism

In a typical freeze-drying process, a liquid sample is first frozen by contacting with or immersion into a cold bath. Then in the following drying process, the frozen solvent inside the sample is removed by sublimation under vacuum. Meanwhile the sample remains frozen at a temperature below its glass transition temperature or melting point [146, 147]. Thus, the porous structure of the obtained sample is formed by the space occupied by solvent crystallisation, and the solvent crystallites behave as pore-forming templates.

Apparently, the freezing process is crucial for producing samples with desirable porous structures. In the freezing process, solvent crystallises while the solute is excluded from the solvent crystallites due to the low solubility of impurities in crystallites. As a result, the solute concentration in front of the solvent crystallites is increased forming a supercooled zone, and the solvent crystallites grow by breaking down the planar interface [148-151]. The crystallisation process of the solvent molecules is controlled by varying the freezing conditions, such as freezing temperature, freezing direction, solution concentration and nature of solvent and solute. All these parameters will affect the ultimate porous structure of the produced material, and will be discussed in the following sections.

In a traditional freeze-drying process, the drying process includes two steps, i.e. primary drying and secondary drying. In the primary drying step, the frozen solvent crystallites are removed by sublimation, whereas in the secondary drying step, the unfrozen solvent bound to the polymer is desorbed at a lower vacuum level than that in the primary drying step [144]. Thus, the desirable porous structure formed in the freezing step could be successfully maintained due to the low surface tension involved in the freeze drying process. While in the normal drying process, the high capillary force or surface tension would normally cause the collapse of the pore structure [145].

2.4.2 Influencing Factors

As mentioned above, the freeze drying method employs solvent crystallisation to produce pores, and the solvent crystallites serve as pore-forming templates. Consequently, the

ultimate pore structure will be influenced by controlling the freezing conditions including freezing temperature, freezing direction, solution concentration, and nature of the solute and the solvent. For example, the mean pore size could be reduced by increasing the solution concentration while keeping other freezing parameters unchanged [152, 153].

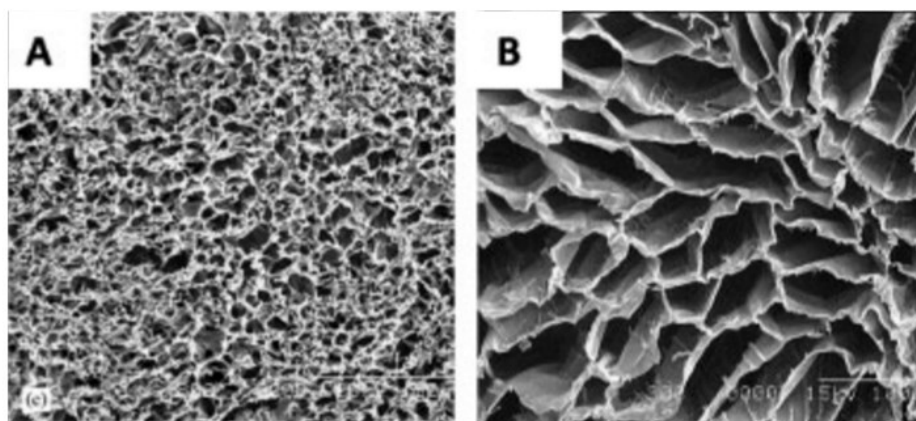


Figure 2.17 SEM images of porous chitosan scaffold prepared by freezing the chitosan solution in (a) liquid nitrogen and (b) dry ice [152]

Apart from increasing the solute content, the mean pore size of the material prepared by the freeze drying method is decreased by reducing the freezing temperature. For example, Madihally and Matthew prepared chitosan scaffolds by freezing the chitosan aqueous solution at -20°C , -78°C and -196°C [152]. The SEM images of the porous chitosan scaffolds are displayed in Figure 2.17. When the chitosan solution was frozen in liquid nitrogen at an extremely low temperature of -196°C , the nuclei formation of ice took place rapidly leading to the formation of small crystallites and thus a small pore size. When the freezing temperature was increased to -78°C by employing dry ice as the freezing bath, the formation rate of ice nuclei was slowed down and further growth of ice crystallites occurred leading to an increase in the ultimate pore size.

On the other hand, the pore morphology is significantly affected by the freezing direction. Ordered porous structure can be achieved by orientating the growth of solvent crystallites in one direction, which is called directional freezing [154] or unidirectional freezing [155]. In the unidirectional freezing process, a temperature gradient is applied by moving the sample towards the freezing bath at a controlled rate, or simply contacting one side of the sample with the cooling source. Then the solvent crystallites would grow orderly from the low-temperature end to the high-temperature end, and thus unidirectional pores would be formed after removing the solvent. Figure 2.18 represents the schematic of a unidirectional freezing

process. Solvent crystallites grow from the bottom to the top as the temperature increases, while solutes are expelled and solidify around the solvent crystallites. Subsequently, aligned porous structure will be obtained after removal of the orientated solvent crystallites. In some cases, bridges between crystallites may be formed due to the solutes trapped within the growing solvent crystallites [140, 141].

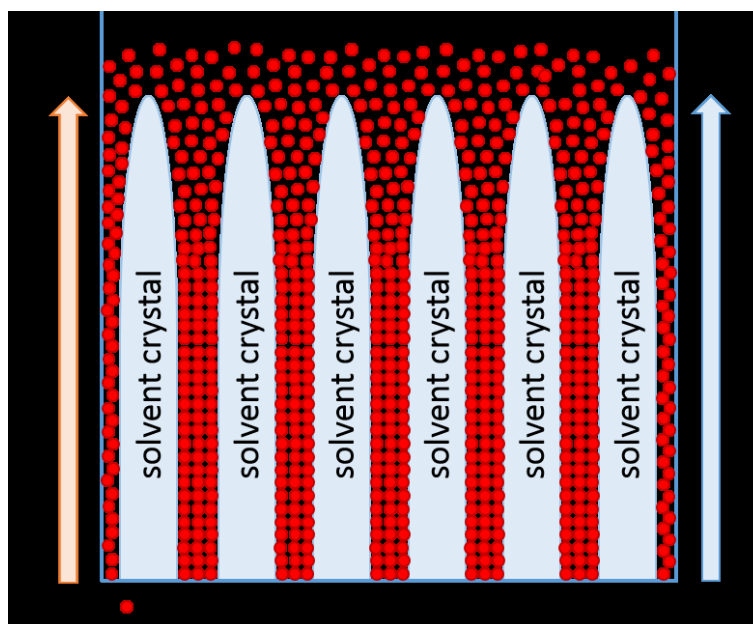


Figure 2.18 Schematic of unidirectional freezing process (adapted from [154])

Besides, porous particles could be formed by the spray freezing method. In this method, the feed solution is pumped into the cryogenic liquid under a constant high pressure and is atomized immediately into microdroplets frozen in the cryogen [156]. Porous microparticles are then obtained by separating the frozen microdroplets and removing the solvent in a freeze-drying process.

In conclusion, various porous and particulate structures (e.g. aligned porous structure, microwires and nanowires, microparticles and nanoparticles) can be produced via the freeze-drying method from a wide range of materials, including polymers, proteins, pharmaceuticals, metals and ceramics in different conditions (e.g. solutions, emulsions and colloidal suspensions) [145].

2.4.3 Potential in Membrane Preparation

Because of the easy control and versatility of the freeze drying method, it has shown great potential in large-scale production of materials with defect-free uniform structure, hierarchical porosity and excellent mechanical strength, such as membranes. As discussed in

the beginning of Section 2.4, only a few attempts have been made to prepare PVDF membranes using this freeze-drying method. Due to the lack of effective control of the crystallite size, however, the attempts failed to produce membranes with pore size smaller than 250 nm [137, 157], which is far from the most preferred pore sizes (20-100 nm) of PVDF membranes.

In the practice of the freeze-drying approach, the actual nuclei/crystallite sizes obtained are determined by the kinetics of nucleation/crystallisation during the transient cooling stage [158]. The size and size distribution of the crystallites are dramatically affected by the cooling rate. With a fast cooling rate, the size will be small and the size distribution will be narrow, and vice versa [158]. On the other hand, during the late stage of crystallisation, small individual crystallites will agglomerate to form big grains, which is called the coarsening process. To achieve small crystallites and thus small pores in the final membranes, it is important to get small crystallites at the first place. It is also crucial to constrain further growth of small individual crystallites during the late stage, especially to prohibit their agglomeration. The second challenge is much more difficult to tackle, and to our best knowledge, has not been well solved by other researchers.

2.5 Summary

In this chapter, the attractive properties of PVDF as a membrane material has been introduced, followed by detailed discussions on the mainstream preparation techniques of PVDF MF/UF membranes and recent developments on the membrane modification approaches. The membrane defects caused by the preparation techniques and the drawbacks of the modification methods have also been pointed out. To deal with these issues, the “freeze drying” approach in materials engineering has been introduced and shows great promise as a brand new concept for membrane manufacturing procedures.

Recently, membrane technology has attracted increasing attention in water and wastewater treatment compared to other conventional technologies. PVDF is one of the most commonly used materials in the preparation of MF and UF membranes. This is because PVDF has several outstanding properties, such as thermal stability, chemical resistance, mechanical strength and solubility in organic solvents. In fact, PVDF membranes have been successfully commercialized for decades and widely applied in MBR, water purification in potable water plants, pre-treatment in desalination plants, and wastewater recovery for industrial applications.

Nowadays, in both laboratory research and industrial manufacturing processes, PVDF MF/UF membrane are mainly produced by the phase inversion technique. Since PVDF is a

semi-crystalline polymer, the phase inversion process of PVDF in the membrane formation process is determined by the combination of liquid-liquid demixing and polymer crystallisation. Consequently, various parameters are involved affecting the ultimate membrane morphology, properties and performance. Generally, the PVDF membranes produced by the phase inversion technique have an asymmetric structure, which is composed of a dense skin layer with finger-like voids underneath, and a sponge-like supporting layer with or without macrovoids. The presence of the finger-like voids and macrovoids are adverse to the membrane mechanical strength, especially when applied in high-pressure treatments. Moreover, the low surface porosity on the dense skin layer contributes to high membrane resistance and thus low water permeance, although it is beneficial for the membrane selectivity.

Besides, due to the hydrophobic nature of the material, membrane fouling is normally inevitable, particularly when PVDF membranes are applied in the treatment of wastewater containing organic compounds. Various modification techniques therefore have been developed to improve membrane hydrophilicity, enhance membrane permeability and reduce membrane fouling. However, to the best knowledge of the authors, all the modification methods involve extra chemicals or pre/post-treatment, which in turn increase the membrane production cost.

On the other hand, freeze drying method is one of the most commonly used techniques for preparing porous materials in materials engineering. In the freezing process of a liquid sample, solvent crystallisation takes place repelling the solute from solvent crystallites. The solvent crystallites will be removed in the following drying process to form a porous structure. Thus, solvent crystallisation is employed to generate pores, and the resultant porous structure is affected by cooling conditions. Theoretically, membranes with aligned pores of desirable pore size and pore size distribution could be obtained by effective control of the cooling conditions in the freeze drying process of the dope solution.

2.6 References

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Chapter 3 PVDF/Palygorskite Composite Ultrafiltration Membranes with Enhanced Abrasion Resistance and Flux

3.1 Abstract

The anti-wearing property is important to the lifetime of membranes especially when they are used in heavy-duty water treatment, where the content of suspended solid is often high. Abrasion-resistant membranes are expected to have prolonged lifetimes and reduce considerably the maintenance cost of water treatment plants. In this research, palygorskite (PGS), a natural abundant nano rod-like clay material with hydrophilic properties and excellent mechanical strength, was used as the reinforcement filler in poly(vinylidene fluoride) (PVDF) ultrafiltration membranes to improve the anti-wearing property. The prepared membranes were subjected to a series of characterisations to investigate membrane structure, surface hydrophilicity, filtration performance and mechanical strength. A simple, quantitative methodology was also proposed to assess the abrasion resistance of the membranes, aiming to establish a feasible and reliable testing protocol in the laboratory. It is found that the PGS readily improves the membrane tensile strength, Young's modulus and abrasion resistance to SiC particles, whilst the permeability of the membranes increases without sacrificing selectivity. Particularly, the addition of 10% PGS leads to a drastic increase in abrasion resistance, with the abrasion rate reduced to 1/170 of the unreinforced membrane, which could be attributed to the transition of abrasion from a ductile manner to a brittle manner. Moreover, the 10 wt.% PGS reinforced membrane shows increased permeation flux from 106.1 L/m²h (LMH) to 282.5 LMH, and the dextran molecular weight cut-off (MWCO) was maintained at a level of 150 – 200 kDa.

3.2 Introduction

Poly(vinylidene fluoride) membranes have attracted much attention from researchers and industrial manufacturers for many years due to their excellent thermal and chemical resistance as well as high mechanical strength, and they have been widely utilized in the applications of industrial secondary effluent treatment and other ultrafiltration processes for water purification [1-3]. The PVDF material can be easily dissolved in several common organic solvents including *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), triethyl phosphate (TEP), etc. [4], which enables low-cost production of PVDF membranes using the simple and economical phase-inversion technique [3]. Despite those advantageous properties,

current PVDF membranes still encounter important issues during long-term operation, and one of these issues is the wearing of membranes, which is normally inevitable in applications of water/wastewater treatments. In filtration processes, the abrasive materials, mainly suspended particles in the feed solution, compresses and grinds the membrane surface under the operating pressure with a high flow rate [5]. The wearing problem compromises the stability and durability of PVDF membranes in water/wastewater treatments, especially when solid content is high, and thus abrasion-resistant membranes will be meaningful for extending the lifetime of membrane modules.

Although little research has been carried out directly on the anti-wearing property of membranes [6-8], numerous approaches have been explored to modify PVDF membranes in order to improve their mechanical properties, which is crucial to the anti-wearing performance. Among various modification methods, blending inorganic nanoparticles in the polymer solution has been extensively studied due to its simplicity and effectiveness in improving both mechanical and performance characteristics [3]. Among those mentioned, clay nanoparticles have been popular since they are naturally abundant, and consequently, cost-effective. The most commonly used clays in the preparation of polymer-clay nanocomposite membranes are montmorillonite (MMT) and modified MMT, and most of these studies so far focus on the improvement of water permeability, anti-fouling property and mechanical strength [9, 10]. In addition to these studies, Lai et al. have conducted a series of systematic studies particularly on the effect of nanoclay addition on the abrasion resistance of PVDF membranes [6-8]. In their work, the effectiveness of various methods on the dispersion of commercial MMT nanoclay in NMP was investigated [6], then PVDF/MMT composite membranes were prepared in two geometries, i.e. hollow fibres and flat sheets. The two types of PVDF nanocomposite membranes were subjected to two specially-designed accelerated abrasion tests in order to evaluate their abrasion resistance [7, 8]. One method was to use abrasive suspensions to wear the outer surface of the hollow fibres and then observe the change in bubble points; the other one was to directly abrade the flat-sheet membranes against sandpapers and then measure the change in the weight. Although these indirect measures were difficult to give quantitative results that directly link to abrasion resistance due to the porous and inconsistent membrane structures, they were able to give qualitative analysis. The results of the abrasion tests indicated that the PVDF/MMT composite membranes had better abrasion resistances as they showed a slower abrasion rate than that of a pure PVDF membrane.

Despite the enhanced abrasion resistance in both of Lai's previous works, it has been found that the water permeability decreased considerably due to the addition of MMT nanoclay. Apart from commercial MMT and modified MMT, Zhang et al. modified PVDF membranes with another commercial nanoclay, palygorskite, also known as attapulgite [11]. The PGS was first modified with a silane coupling agent, and then incorporated into PVDF solutions in DMAc with polyvinylpyrrolidone (PVP) as the pore-forming agent. The authors found that the modified PGS improved not only hydrophilicity, water permeability of the membranes, but also the anti-fouling performance. However, they didn't report the mechanical property and abrasion resistance of the PGS modified membranes.

In this work, PGS nanoclay is used directly (without modification) as the filler in order to produce reinforced PVDF ultrafiltration flat sheet membranes with improved mechanical strength and abrasion resistance without compromising the filtration performance. In contrast to Zhang's study, we use TEP as the solvent rather than DMAc since PVDF membranes prepared from the PVDF/TEP/water system normally has a typical bi-continuous structure with interconnected pores [4, 12, 13]. More importantly, after comprehensive structural and performance characterizations, we propose to use a simple and straightforward method to evaluate the anti-wearing property of membranes, which is able to provide more reliable and quantitative results. The results show a drastically improved abrasion resistance and a transition of the erosion mode of the reinforced membranes, which was not revealed before.

3.3 Methodology

3.3.1 Materials

Commercial PVDF (Kynar®K-761, $M_w = 440,000$ Da, $\rho = 1.79$ g/cm³) was purchased from Elf Atochem. Palygorskite nanoclay (99.8% purity, $\rho = 2.05$ g/cm³) was supplied by Jiangsu Jiuchuan Nano-Material Technology Co., China. PGS is a natural clay mineral abundant all over the world; in particular, China has 60% of the world's reserves, hence it is readily available at low cost. The theoretical formula of PGS is $(Mg,Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$ with a pleated layered structure comprising of continuous $(Si,Al)_2O_5$ sheets linked by octahedral ribbons (Mg,Al) , which are very sharp and chainlike, and form channels. PGS has a very hydrophilic surface due to the existence of three kinds of water components within its structure including zeolitic water in channels, coordinated water bonded to Mg and hydroxyl water (-OH). The PGS powder used here is nanorod-like crystalline with high degree of crystallinity and uniform size distribution with diameters between 20 and 50 nm and length

ranging from 500 to 1500 nm. Both the PVDF powder and PGS powder were dried at 80 °C for 24 hours before use. PEG-400 ($M_w = 400$ Da), TEP, dextran of different molecular weights (10,000 - 150,000 Da) and silicon carbide (SiC, 200 - 450 mesh) were purchased from Sigma-Aldrich, UK and were used as received.

3.3.2 Membrane Preparation

PVDF/PGS composite membranes with various PGS loading amounts and pure PVDF membrane as a control sample were prepared via a combined non-solvent induced phase separation (NIPS) and thermally induced phase separation (TIPS) process, in which the phase inversion was introduced by the exchange of solvent (TEP) and non-solvent (water) together with a temperature difference. Various compositions of the dope solutions were summarised in Table 3.1.

Table 3.1 Compositions of the PVDF/PGS/PEG/TEP dope solutions with various PGS loadings

Sample	PVDF (g)	TEP (g)	PEG-400 (g)	PGS (wt.%) ^a
AT-0	20	80	5	0
AT-0.5	20	80	5	0.5
AT-1	20	80	5	1
AT-4	20	80	5	4
AT-7	20	80	5	7
AT-10	20	80	5	10

^a: The percentage is relative to the weight of PVDF.

In the preparation of the dope solutions, calculated amounts (0, 0.5, 1, 4, 7 and 10 wt.% based on the weight of PVDF powder) of PGS nanoclay were first dispersed in TEP under ultrasonication (VWR USC300T Ultrasonic Cleaner, 45 kHz, 80 W) for 3 hours to obtain a uniform suspension. Then an appropriate amount of PVDF powder (19.05 wt.%) was added to the suspension and the mixture was stirred at 80 °C for 24 hours to ensure that the polymer was completely dissolved. Subsequently, 4.76 wt.% of PEG was added and the mixture was stirred at 80 °C for another 24 hours for complete mixing. Finally, the PVDF/PGS/PEG/TEP dope solution was left in the oven at 80 °C overnight for degassing.

Table 3.2 Casting conditions for preparing the flat sheet membranes

Room temperature	20 ± 1 °C
Relative humidity	35 ± 1 %
Casting thickness	150 µm

Casting speed	4 cm/s
Casting temperature ^a	80 °C
Evaporation time	5 s
Coagulation bath ^b	Ultrapure water
Coagulation bath temperature	21 ± 1 °C

^a: The hot plate of the casting machine, the glass plate and the casting knife were pre-heated to 80 °C.

^b: The coagulation bath was filled with ultrapure water produced from a reverse osmosis system from Collins Water Products.

The PVDF/PGS composite membranes were then prepared by casting the dope solution onto a glass plate at 80 °C before being immersed in a water coagulation bath at 20 °C in a room with constant temperature and humidity. The fabricated membrane was then kept in deionised water, which was changed frequently to remove the residual solvent before characterisations. Table 3.2 shows the casting conditions for preparing the flat sheet membranes.

3.3.3 Membrane Characterisation

The wet membranes were used directly for porosity and pore size measurements, abrasion tests and filtration tests, but were dried via solvent (ethanol) exchange technique at room temperature prior to other characterisations.

3.3.3.1 Membrane Morphology

The morphologies of the membranes including top surface (water side), bottom surface (glass side) and cross section were observed by a scanning electron microscope (SEM, LEO Gemini 1525 FEGSEM, Tokyo, Japan). To obtain samples for the cross section, the wet membrane was first immersed in ethanol for 30min to replace water inside the pores, and then was fractured in liquid nitrogen. The dried surfaces and cross section of each membrane sample were coated with chromium of 10 nm thickness using an Emitech K550 ion sputtering device prior to the test.

3.3.3.2 X-Ray Diffraction (XRD) Analysis

The crystalline structure of all the membrane samples and the PGS nanoclay sample were determined using an X-ray diffractometer (X'Pert PRO Diffractometer, PANalytical) with a source intensity of 40 kV / 40 mA. All the samples were characterised in the scanning range of $5^{\circ} < 2\theta < 50^{\circ}$.

3.3.3.3 Hydrophilicity, Porosity and Pore Size Measurements

The surface hydrophilicity of the membranes was studied by measuring the water contact angle of the membrane top surface. The measurement was conducted at room temperature using a Drop Shape Analyser (DSA 10 MK2, Krüss GmbH, Hamburg, Germany). In the test, 20 μL of deionised water droplets were deposited onto the top surface of dry membrane samples. The image was taken and the contact angle was measured from shape analysis. At least five independent readings were taken at different sites on each membrane sample and the average value was reported.

The porosity of each membrane sample was determined by a weight-loss method. Wet membranes with weight around 110 mg were swung vigorously to remove the water on the exterior membrane surface prior to determining the exact mass. The wet sample was then left in ambient air (22 °C, humidity of $\sim 60\%$) for overnight to dry completely. The weight of the membranes was monitored to be constant after drying for one hour under such conditions. The porosity was calculated using the following equation:

Equation 3.1
$$\varepsilon = \frac{(m_1 - m_2)/\rho_w}{(m_1 - m_2)/\rho_w + m_2/\rho_m} \times 100\%$$

where ε is the volumetric porosity of the membrane sample; m_1 and m_2 are the weights of the wet membrane and dried membrane, respectively; ρ_w is the density of water, which is 1 g/cm^3 ; and ρ_m is the density of membrane, which is calculated based on the volume ratio of PVDF and PGS in the membrane and each density respectively. For each membrane, three different samples were tested and the average value was recorded.

The average pore size and pore size distribution of each membrane sample were determined by the gas-liquid displacement method [14] using a capillary flow porometer (CFP 1500A, PMI), where nitrogen is used to repel water in the pores of a pre-wetted membrane sample [15-17], and the applied pressure and corresponding gas flow rate were recorded. Then the membrane pore size was calculated according to the Young-Laplace equation shown below:

Equation 3.2
$$\Delta p = \frac{4\gamma \cos \theta}{d_p}$$

where Δp is the applied pressure, d_p is the pore diameter, γ is the surface tension of water and θ is the water contact angle of the membrane surface.

3.3.3.4 Permeation Testing

In order to evaluate the filtration performance of the membranes, pure water flux (PWF) and dextran MWCO measurements were conducted using a 400 mL dead-end filtration cell (Stirred Cell Model 8400, Merck Millipore, Germany). In each test, the wet membrane sample was compacted at 2 bars with deionised water for 30 minutes before measurements were taken at 1 bar.

The PWF was calculated based on the equation shown below:

Equation 3.3
$$J = \frac{V}{A \times t}$$

where J is the flux (L/m²h), V is the permeate volume (L), A is the effective membrane area (m²) and t is the time of permeate collection (h). Five readings were taken in order to give an average value.

After the PWF test, an aqueous solution of dextran mixture was used with stirring at 300 revolutions per minute (RPM) to determine the membrane MWCO. Samples of the permeate were taken after 30 minutes of filtration. High performance liquid chromatography (HPLC) with refractive index (RI) detector (Shimazu, Japan) was used to analyse the concentrations of each dextran in the permeate and feed samples. The dextran rejection ($R_{dextran}$) was calculated based on the following equation:

Equation 3.4
$$R_{dextran} = \left(1 - \frac{c_p}{c_f}\right) \times 100\%$$

where c_p and c_f are the concentrations of each dextran in the permeate and the feed solution, respectively. The rejection coefficients of different dextrans in the mixture were plotted into a curve for each sample. And the membrane MWCO was reported as the dextran molecular weight at which $R_{dextran} \geq 90\%$.

3.3.3.5 Mechanical Testing

Mechanical properties of the membranes were tested according to American Society for Testing and Materials (ASTM) D882 using a tensile testing machine, Lloyd EZ 50. The samples were cut into 10 mm wide parts and the thickness was measured under SEM. Each sample was initially fixed at a gauge length of 50 mm and was then stretched at a constant rate of 10 mm/min; corresponding tensile force was recorded by a transducer. The elongation ratio and tensile strength at the breaking point and Young's modulus were measured. At least 5 samples were tested for each membrane and the averaged value was recorded.

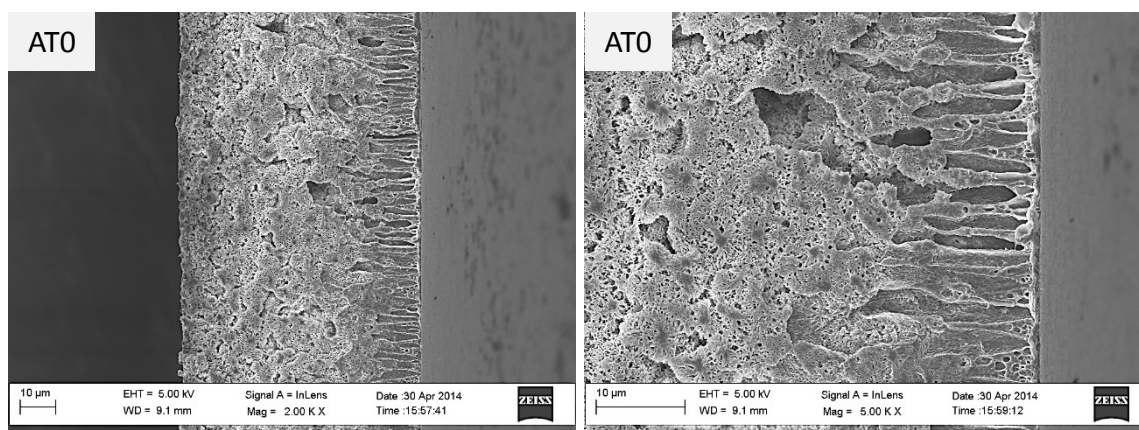
3.3.3.6 Abrasion Resistance Testing

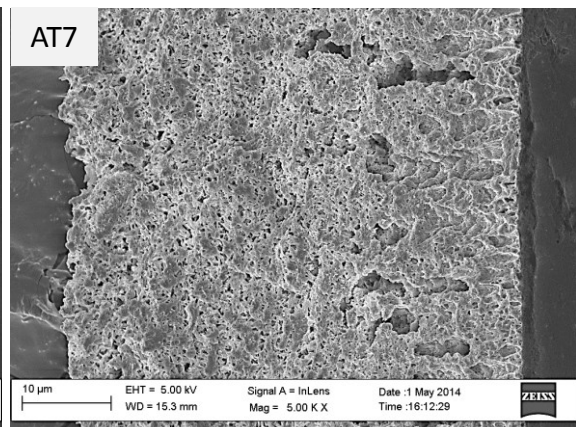
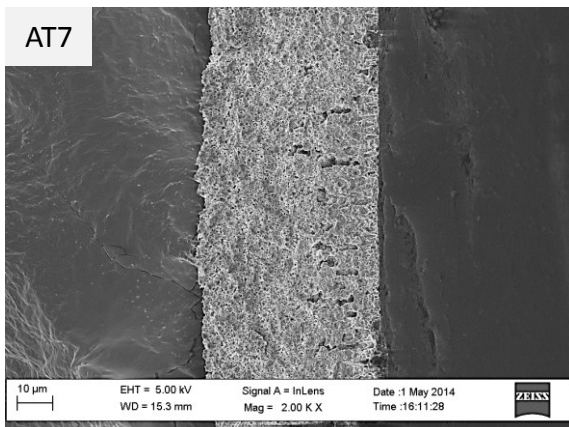
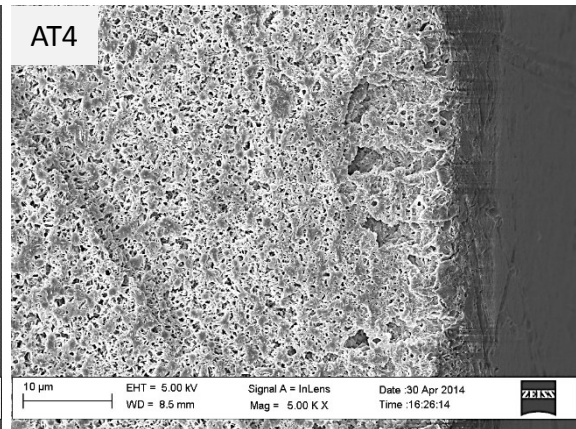
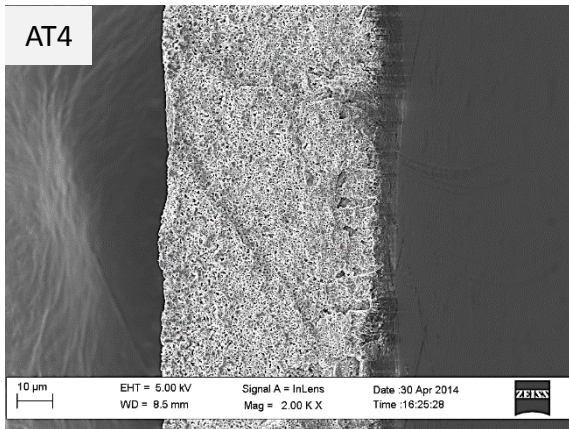
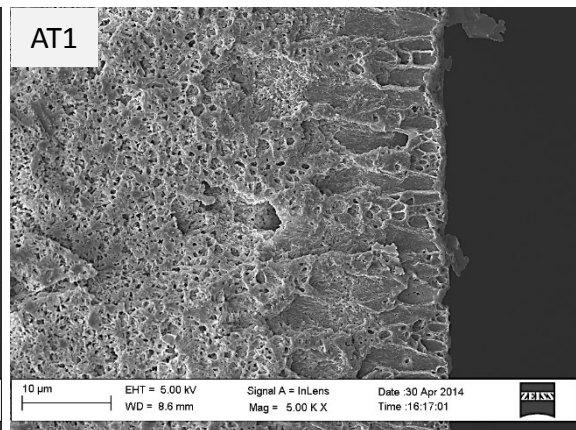
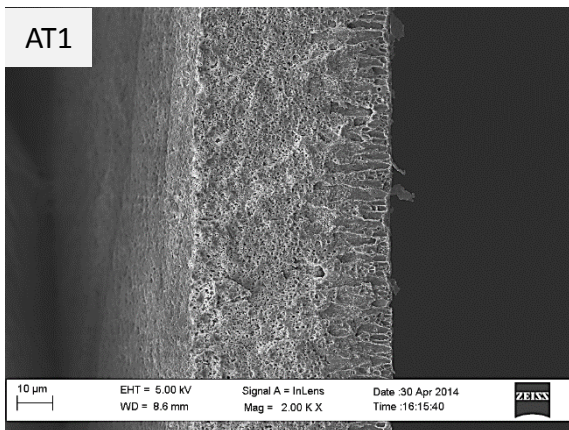
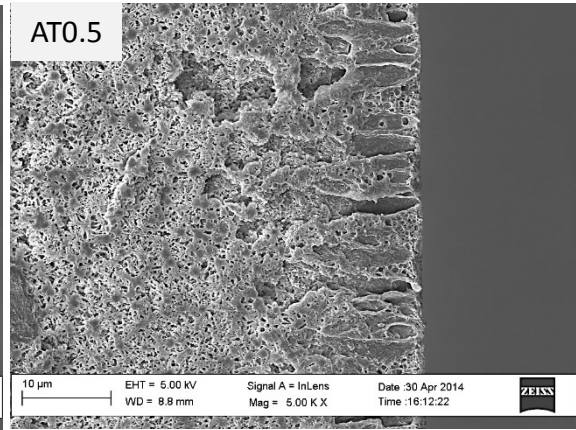
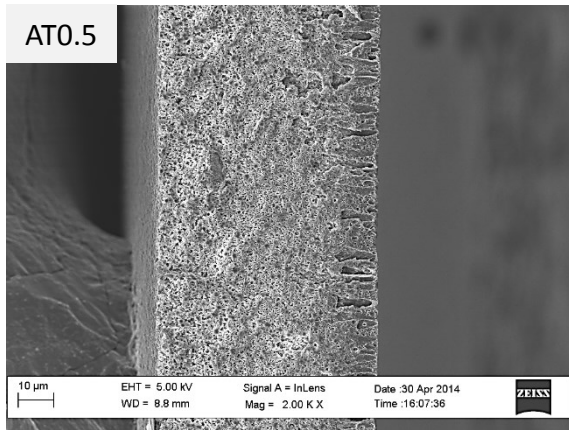
As mentioned in the introduction section, the abrasion test of flat sheet membranes has only been conducted by Lai et al. [8]. In their work, the abrasion test was conducted with a Martindale Wear & Abrasion Tester, and the weight loss of membrane samples due to abrasive wearing was monitored during the test. However, specific equipment was required in such a test and the weight loss was not accurate enough since the worn membrane debris may stick to the membrane during weighing and cause errors. In this work, the abrasion test was carried out using the stirred cell employed in the filtration tests. The total suspended solid in most kinds of wastewater varies from 200 mg/L to 2000 mg/L depending on the source of wastewater [18]. Therefore, a silicon carbide suspension with SiC content of 2000 mg/L was prepared and used to simulate an accelerated abrasion condition in wastewater treatment. The wet membrane sample was placed in the filtration cell, and 300 mL of the SiC suspension was filled and then stirred at 400 RPM for 48 hours. Subsequently, the membrane sample was washed under ultrasonication for 10 min to remove all debris worn away from the membrane during the test. Then the change in the membrane cross section structure was observed using SEM, and the membrane thicknesses at the centre, 1 cm radius, 2 cm radius and 3 cm radius of the membrane were measured at the same time.

3.4 Results and Discussions

3.4.1 Membrane Structure

3.4.1.1 Morphological Structure





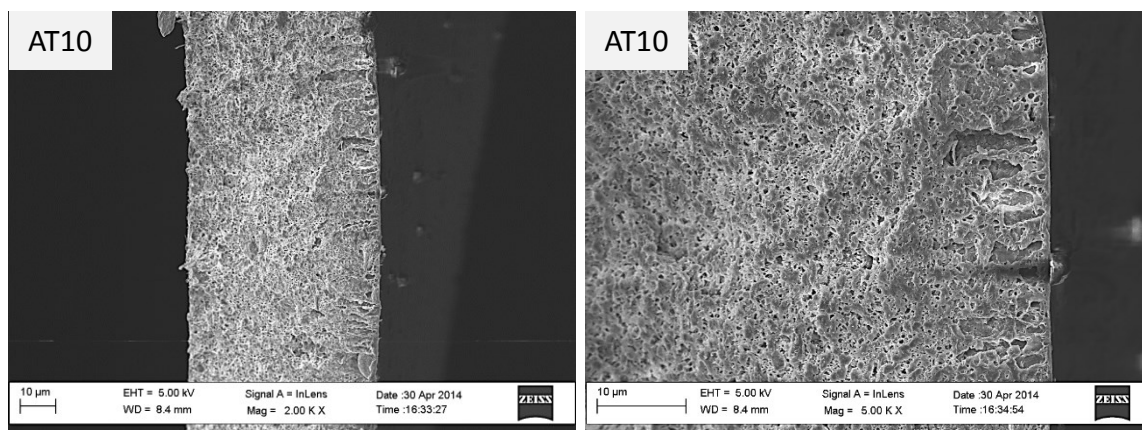
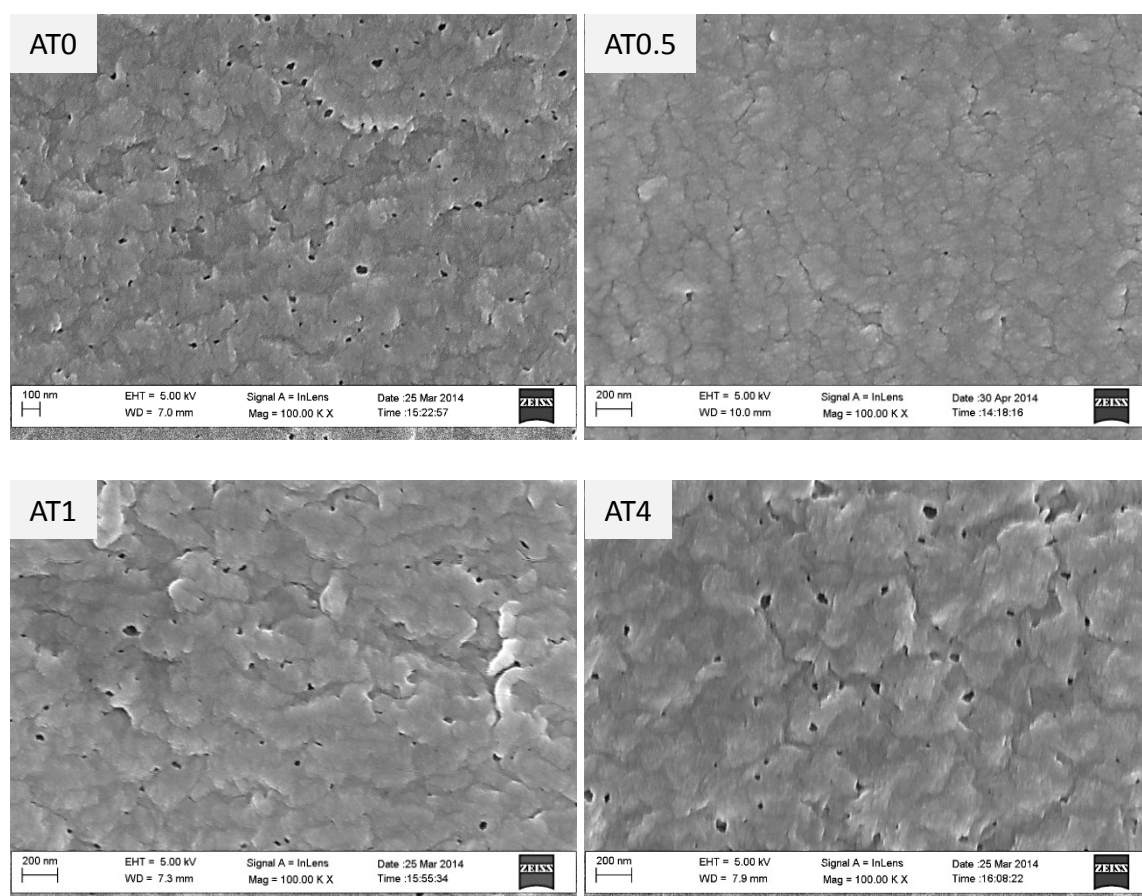


Figure 3.1 SEM images of the cross sections of Samples AT0 - AT10: (left) overview and (right) high magnification image of the finger-like structure

In order to investigate the effect of PGS addition on the membrane morphology, SEM images of the cross section, top surface and bottom surface of the membranes with different PGS loadings were obtained and shown in Figure 3.1, Figure 3.2 and Figure 3.3, respectively.



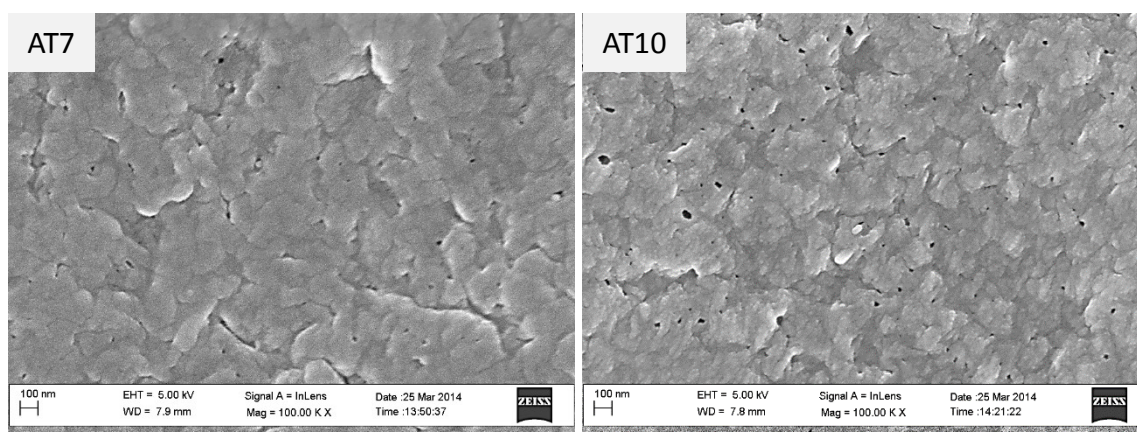
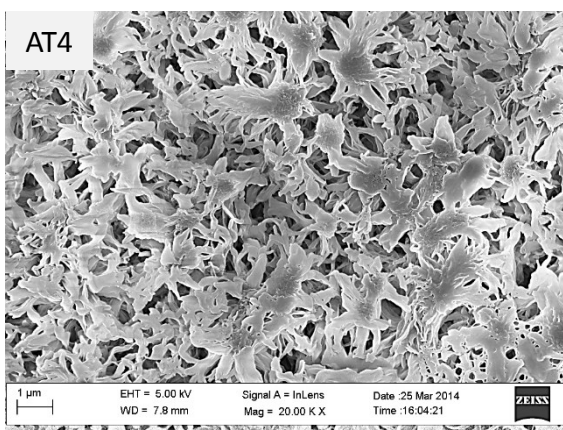
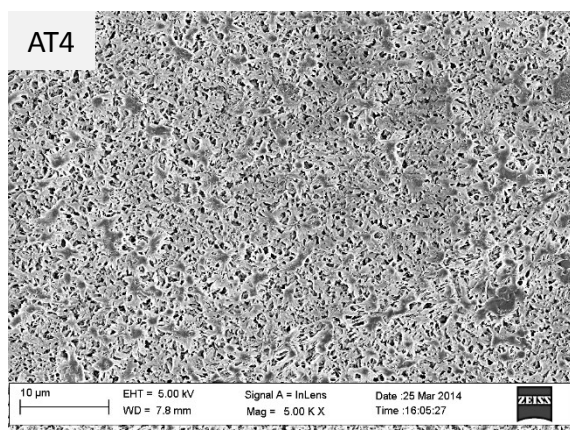
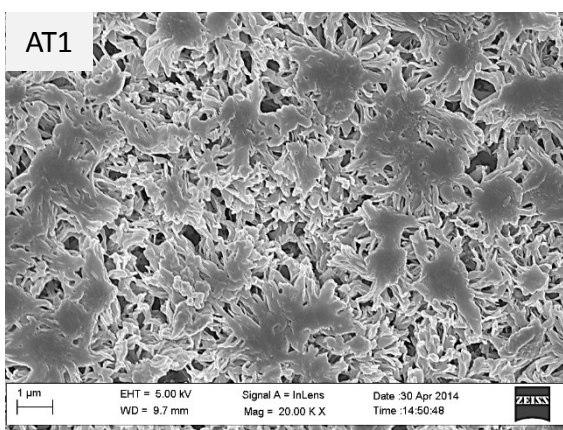
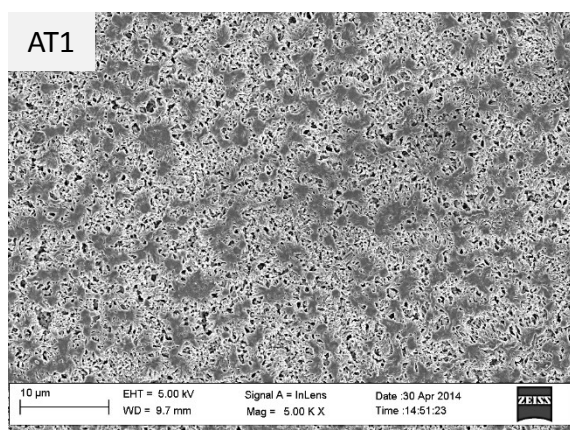
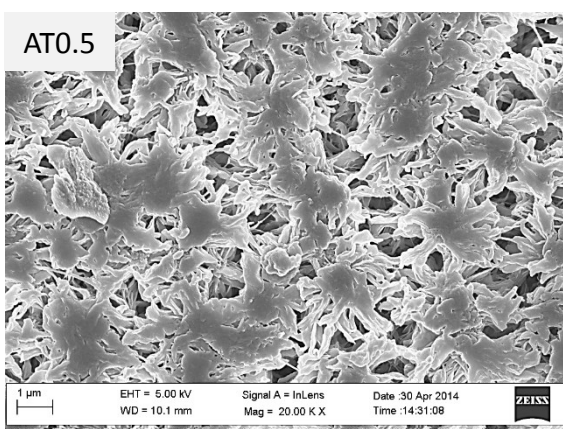
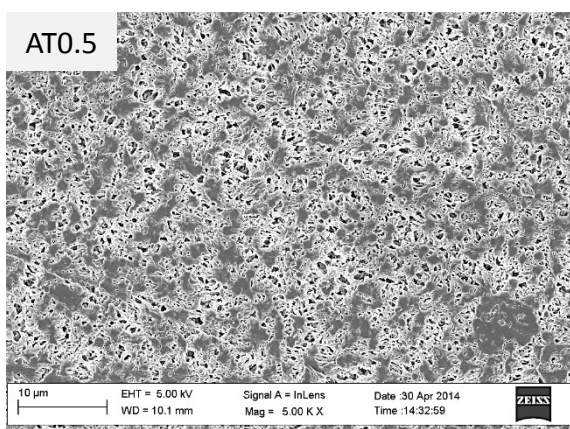
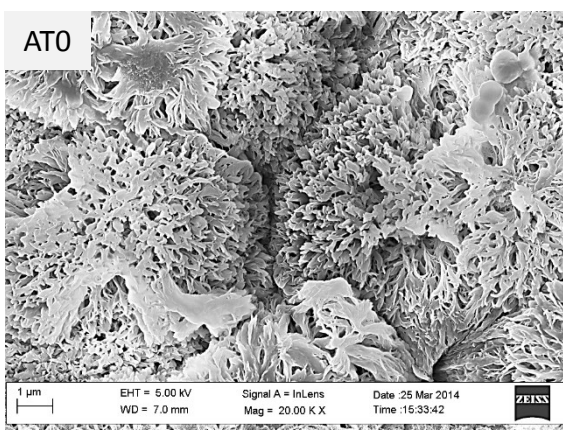
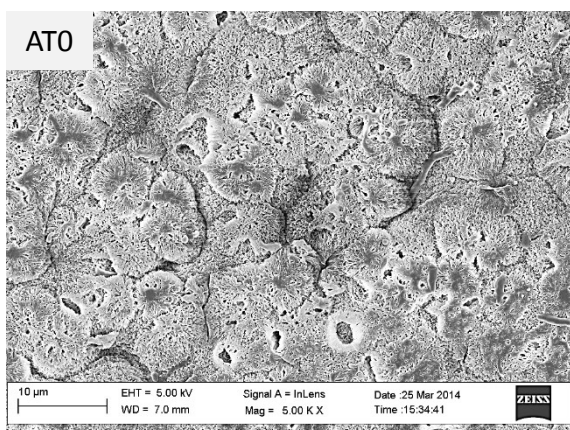


Figure 3.2 SEM images of the top surfaces of Samples AT0 - AT10

As can be seen in Figure 3.1 and Figure 3.2, all the membranes with or without PGS addition have an asymmetric structure with a skin layer and a bi-continuous interconnected support layer. The skin layer has a nano-porous morphology, and short parallel finger-like voids (shorter than one-third of the membrane thickness) were formed underneath the skin layer. Such morphologies with finger-like voids were probably caused by the addition of PEG, which is known as one of the hydrophilic polymer additives commonly used in the preparation of polymeric membranes via phase inversion methods. The presence of PEG in the polymer solution boosted the exchange of the solvent TEP and the non-solvent water, which increased the tendency of developing finger-like voids, as suggested by various theories regarding finger formation [19]. Then, water invaded into the casting film and developed into the finger-like domains. Figure 3.2 clearly shows pores on the membrane surface with typical sizes ranging from 10 to 40 nm. The pore size varied with different PGS loadings, and Sample AT4 was the largest among the six membranes, which will be further discussed in the following sections. The nanopores on the membrane surface were entrances of the finger-like voids, which are commonly deemed as defects in an ideal membrane. However, in this study, since the finger entrances are small enough to enter the loose ultrafiltration region, they are useful for separation and might contribute largely to water permeation. During the development of these finger-like voids, crystallisation of PVDF may take place quickly in the polymer-rich phase and then stop the finger-like voids growing further, which constrained the parallel finger-like voids to short length and helped to maintain a proper mechanical property of the membranes.



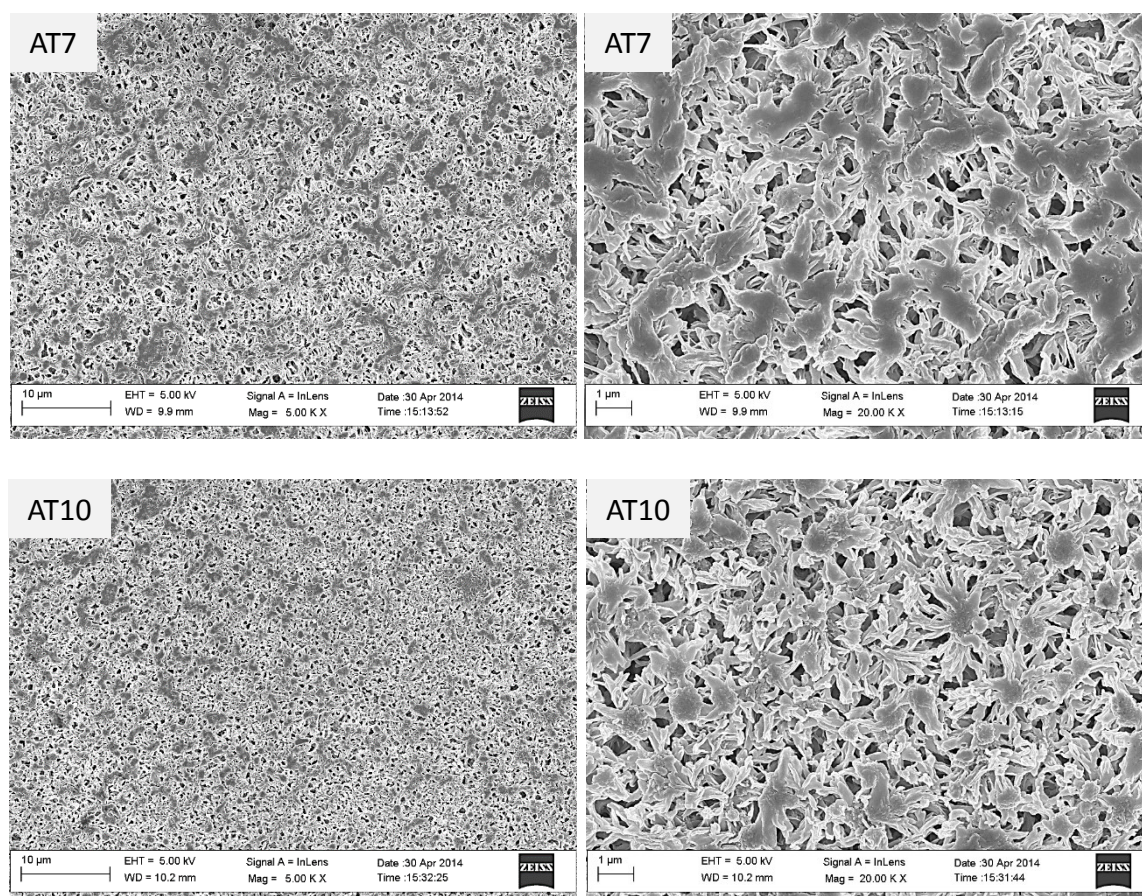


Figure 3.3 SEM images of the bottom surfaces of Samples AT0 - AT10: (a) overview and (b) high magnification image

By adding PGS nanoclays in the polymer solution, the microstructure in the support layer of the membranes became more uniform, and more PVDF crystallines with smaller size can also be observed in Figure 3.1 and Figure 3.3. In addition, the overall membrane thickness and the skin layer thickness were measured from the SEM images of membrane cross-section using ImageJ and are summarised in Table 3.3. It can be observed that, generally, both membrane thickness and skin layer thickness were reduced with the addition of PGS. It is known that the formation of PVDF membranes via immersion-precipitation process is often governed by two types of phase separation events, i.e. liquid-liquid demixing and the crystallisation of PVDF, as PVDF is a semi-crystalline polymer. In this study, PVDF membranes were prepared from polymer solutions containing 20 wt.% PVDF in TEP. According to analysis conducted on the PVDF/TEP/water system by Lin et al. [12], the 20 wt.% PVDF dope solution stays in a metastable state with respect to crystallisation. This means that the crystallisation of PVDF will be triggered immediately after immersion in the water bath. Meanwhile, there was a temperature difference between the casting film (80 °C) and the coagulation bath (20 °C) in the immersion precipitation process. The sudden temperature drop

of the casting film would further facilitate the crystallisation of PVDF. When PGS nanoclays were added into the PVDF solution, they may work as nucleation seeds and increase the number of PVDF crystallites. As a consequence, the size of the PVDF crystal was reduced, which led to a more uniform microstructure. The addition of PGS nanoclay may increase not only the number of PVDF crystallites, but also the PVDF crystallinity of the membranes, leading to higher PVDF density and hence the reduced overall membrane thickness. Besides, it is reasonable to suspect that the enhanced PVDF crystallisation process also increases the phase separation rate at the surface of the polymer solution, which resulted in the decreased membrane skin layer thickness, as commonly observed in polymer membranes when instant phase separation is involved.

Table 3.3 Structural and performance characteristics of Samples AT0 – AT10

Sample	AT0	AT0.5	AT1	AT4	AT7	AT10
Porosity (%)	75.3 ± 0.5	74.2 ± 0.5	74.9 ± 1.3	74.6 ± 1.8	75.2 ± 0.6	76.7 ± 1.3
Overall membrane thickness (μm)	67.5 ± 0.5	61.8 ± 0.5	54.9 ± 1.2	59.9 ± 1.1	49.9 ± 1.3	54.2 ± 0.8
Water contact angle ($^\circ$)	68.5 ± 5.4	67.8 ± 5.2	72.7 ± 4.8	67.9 ± 3.4	71.7 ± 3.2	68.8 ± 5.6
Skin layer thickness (μm)	0.9 ± 0.2	0.5 ± 0.2	0.7 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.6 ± 0.2
Mean flow pore diameter (μm)	0.026 ± 0.003	0.024 ± 0.001	0.031 ± 0.003	0.039 ± 0.003	0.029 ± 0.003	0.025 ± 0.002
Surface pore density (No./ m^2)	2.29×10^{13}	2.13×10^{13}	1.46×10^{13}	1.13×10^{13}	1.58×10^{13}	2.34×10^{13}
Tested PWF (LMH)	106.1 ± 1.7	121.5 ± 1.6	221.1 ± 1.6	238.3 ± 2.4	260.5 ± 5.3	282.5 ± 9.6
Theoretical PWF ^a (LMH)	113.3	142.0	196.8	549.6	296.1	153.0
Dextran MWCO (kDa)	200	150~200	150~200	150~200	150~200	150~200

^a: The theoretical PWF was calculated based on Hagen-Poiseuille pore flow model.

3.4.1.2 Crystal Structure

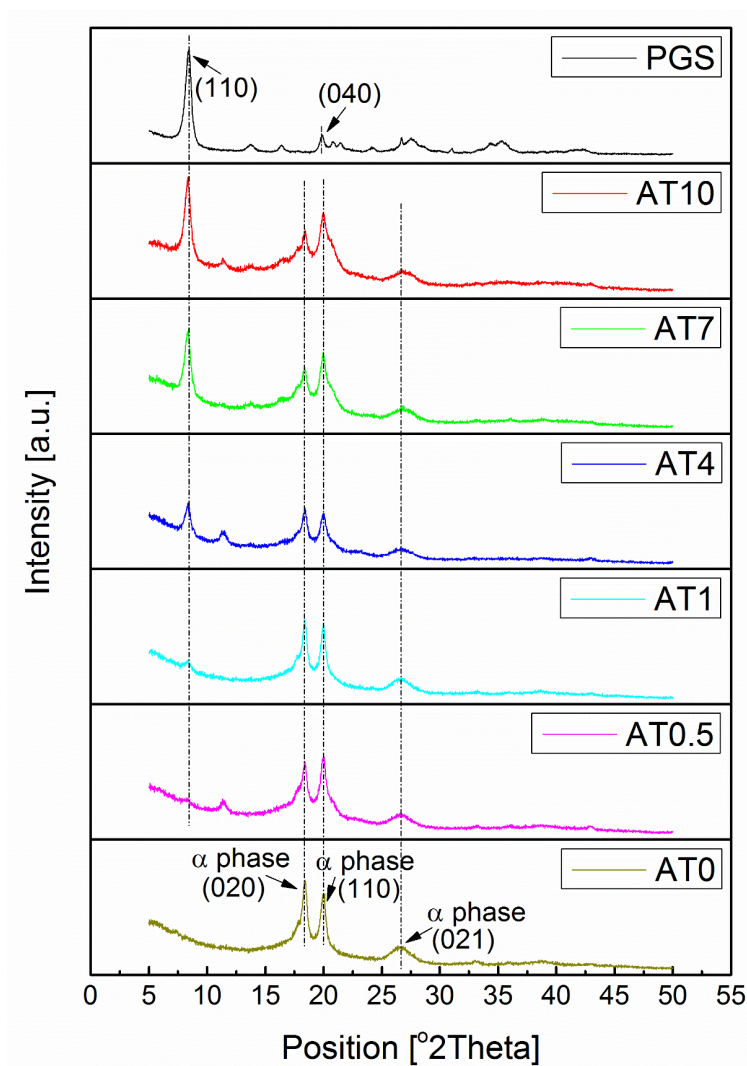


Figure 3.4 XRD patterns of Samples AT0 - AT10

The crystal structures of both the PGS nanoclay and the PVDF polymer were studied using XRD. As shown in Figure 3.4, the PGS nanoclay has a sharp diffraction peak at 8.38° , which also appears in all the PGS reinforced PVDF membranes and the intensity of this peak increases with higher loading amount of PGS. On the other hand, the peaks at 18.44° , 20.07° and 26.75° appeared in all the membrane samples correspond to α -phase PVDF crystal [20]. It can be observed that the intensity of the peak around 20° also increases when more PGS is added, which can be attributed to the overlapping of the 20.07° peak of PVDF and the 19.89° peak of PGS. Generally, the addition of PGS in PVDF dope solution has no effect on the crystal structures of both PGS and PVDF in the prepared membranes.

3.4.1.3 Pore Structure

Apart from morphological study, the pore structure of the membranes was also characterised. Table 3.3 summarises the porosity and the mean flow pore diameter of Sample AT0 - AT10. The porosity of all six samples fluctuates slightly at 75%, whereas their mean pore sizes are in the range from 0.024 μm to 0.039 μm , which are within the range of loose ultrafiltration membranes and close to the size of the surface pores observed in SEM images. Generally, the pore size increases initially along with the addition of PGS nanoclays, reaching the maximum size of 0.039 μm for Sample AT4, and then decreases when more PGS is added. This tendency is also concurrent with the observation of SEM images on the membrane surface. The change in the mean flow pore diameter of the membrane samples could be explained from the formation process of the short finger-like voids underneath the surface. It is assumed that the mean flow pore diameter reflects the size of entrance of the finger-like voids, which is reasonable since the SEM results and porosimetry results show a high similarity. As discussed in Section 3.4.1.1, the formation of the finger-like voids is due to the invasion of water into the casting film when solvent/non-solvent exchange is fast. The mechanism behind this phenomenon can be interpreted as interfacial instabilities, which were proposed by different researchers, though the true origins of the driving force are still arguable [21-25]. As a result of the interfacial tension surrounding the entrance of the nascent fingers, the entrance contracts until the surrounding polymer precipitates, and this finally forms the nanopores on the membrane surface. Therefore, the final size of the nanopores is mainly determined by the competition between contraction and precipitation of the surrounding polymer solution, and the latter is affected by the rates of both solvent/non-solvent exchange and PVDF crystallisation. In this study, the precipitation rate was first increased by adding PGS nanoclays, which acted as nucleation seeds and facilitated the PVDF crystallization process. As such, the mean flow pore diameter of the membranes increased initially, as have been observed in Sample AT1 and AT4. However, when the PGS loading amount became larger, as for Sample AT7 and AT10, the solvent/non-solvent exchange could become considerably slower, because the added PGS nanoclays would result in a more torturous path for the solvent/non-solvent exchange [26, 27]. The slower exchange rate led to slower precipitation and allowed further contraction of the finger entrance, which left smaller pores on the membrane surface.

3.4.2 Membrane Hydrophilicity

The membrane hydrophilicity was evaluated by water contact angle measurement, and the results are shown in Table 3.3. All the membranes show a contact angle around 70°.

Unexpectedly, the addition of PGS didn't improve the hydrophilicity of PVDF membranes, which can occur if the PGS is entirely covered by PVDF and bonds well with the polymer so that such bonding cannot be separated by water. As such, the hydrophilicity on the membrane surface is similar for all the six membrane samples with different PGS loadings. The strong bonding between PGS and PVDF is also indicated by the improvement of Young's modulus, which will be discussed in Section 3.4.4.1.

3.4.3 Filtration Performance

Pure water flux (PWF) and dextran MWCO were tested for all of the prepared flat sheet membranes and the results are listed in Table 3.3. Generally, the addition of PGS nanoclay in the PVDF solution results in a considerable enhancement on PWF. A sharp increase of PWF from 106 LMH to 221 LMH was observed in Sample AT1 compared with Sample AT0. Further increases of PGS addition up to 10 wt% did improve the PWF continuously but the improvement was less significant compared with the change at lower loadings. Zhang et al. [11] also observed similar improvements of PWF in their PGS-modified PVDF membranes. In our case, the improvement of the PWF can be largely attributed to changes in the membrane skin structure as per calculations based on the Hagen-Poiseuille pore flow model:

Equation 3.5
$$\Phi = \frac{dV}{dt} = v\pi R^2 = \frac{\pi R^4}{8\eta} \left(\frac{-\Delta P}{\Delta x} \right) = \frac{\pi R^4}{8\eta} \frac{|\Delta P|}{L}$$

where Φ is the water flux through each pore on the membrane top surface, R is the average pore radius obtained from the porosity measurements, ΔP is the operating pressure (1 bar), η is the viscosity of water at 25°C and L is the thickness of membrane skin layer. It is assumed that the resistance to permeation all came from the skin layer and the nanopores on the membrane top surface were the paths for water permeation. To obtain theoretical PWF, the calculated water flux of each pore was multiplied by the number of surface pores per unit area, which was acquired using ImageJ on the SEM images of membrane top surface.

The results of calculated PWF are summarised in Table 3.3, and they are very close to the experimental results except Sample AT4 and AT10. The discrepancies might be attributed to the uncertainty of three variables, i.e. the pore size (R), the thickness of the membrane skin layer (L) and the number of surface pores per unit area. As shown in the Equation (5), the flux is very sensitive to pore size and a slight change within the data uncertainty could result in a considerable change in permeance. The uncertainty of membrane skin layer thickness is also very significant especially for Sample AT10, as shown in Table 3.3. Furthermore, although the surface pore number was acquired based on at least three SEM images of each sample, the

sample size is still too small to obtain the actual pore density. Apart from the membrane skin layer, other factors such as membrane microstructure in the supporting layer also affect membrane permeability, and they might have been influenced by the presence of PGS nanoclays as well. However, generally, the improvement of the PWF could be attributed to the change in membrane skin layer, which was probably caused by a faster phase inversion/crystallisation rate due to the presence of PGS nanoclays that might act as crystallisation nuclei.

On the other hand, the dextran MWCO of the prepared membranes seems nearly unaffected by the addition of PGS. As shown in Table 3.3, the membrane that was not reinforced has a dextran MWCO of around 200 kDa, whereas the MWCOs of the PGS modified membranes were maintained at the same level even their pore sizes show some variations. One reason for the negligible change in dextran MWCO could be attributed to the use of dextran mixture in the rejection test. According to Tam and Tremblay's study on determining MWCO using a single solute and multiple solutes of varying molecular weights [28], larger molecules could hinder the pathway of smaller molecules due to physical interferences, which results in underestimated membrane MWCO and pore size. Therefore, in this study, the rejection test might not be sensitive enough to reflect the change in membrane MWCO because of the relatively large dextran molecules in the dextran mixture.

3.4.4 Mechanical Properties

3.4.4.1 Mechanical Strength

Table 3.4 Mechanical properties of Samples AT0 - AT10

Sample	Tensile strength (MPa)	Elongation ratio (%)	Young's modulus (MPa)
AT0	3.0 ± 0.3	76.1 ± 10.2	91.1 ± 11.4
AT0.5	3.0 ± 0.3	61.6 ± 19.2	95.4 ± 13.5
AT1	2.7 ± 0.1	44.5 ± 6.1	92.6 ± 10.2
AT4	2.9 ± 0.1	44.9 ± 5.8	104.2 ± 10.0
AT7	3.1 ± 0.1	43.7 ± 2.7	127.1 ± 16.0
AT10	3.5 ± 0.2	46.9 ± 9.7	142.2 ± 22.2

The effects of the PGS addition on a membrane's mechanical properties including tensile strength, elongation ratio and Young's modulus are summarised in Table 3.4. In general, both the tensile strength and Young's modulus of a membrane increase with the addition of PGS, whereas the elongation ratio decreases. In particular, with 10 wt% PGS, the tensile

strength and Young's modulus increased from 3.0 MPa to 3.5 MPa and from 91.1 MPa to 142.2 Mpa, respectively, while the elongation ratio at the maximum load decreased from 76.1% to 46.9%. Similar changes in mechanical properties of nanoclay-modified PVDF membranes have also been observed by Lai et al. [8]. It is worthy to mention that Young's modulus increased linearly with the content of PGS, as shown in Figure 3.5. The linear relation between Young's modulus and the filler content obeys the Rule of Mixtures in composite materials very well [29, 30], which assumes perfect bonding between different components in the composite material. The result indicates that the PGS nanoclay particles were successfully dispersed in the polymer matrix, bonded well with PVDF and played a role as a temporary cross-linker to fasten the polymer chains [31]. This provided toughened local regions in the membrane, which stunted the development of cracks and cavities and hence improved the tensile strength and Young's modulus. As the adverse effect, it also led to the reduction of the elongation ratio.

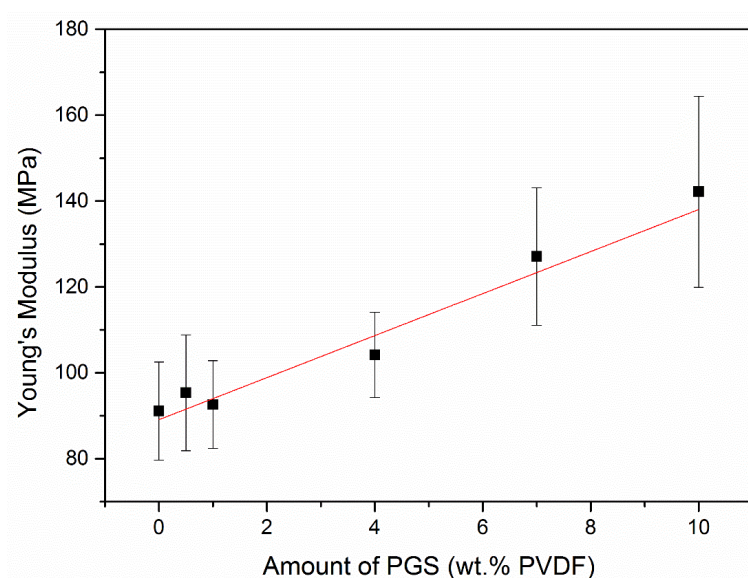


Figure 3.5 Membrane Young's modulus at different PGS loading amounts. The line is the linear fitting result aiming to guide the eye.

3.4.4.2 Abrasion Resistance

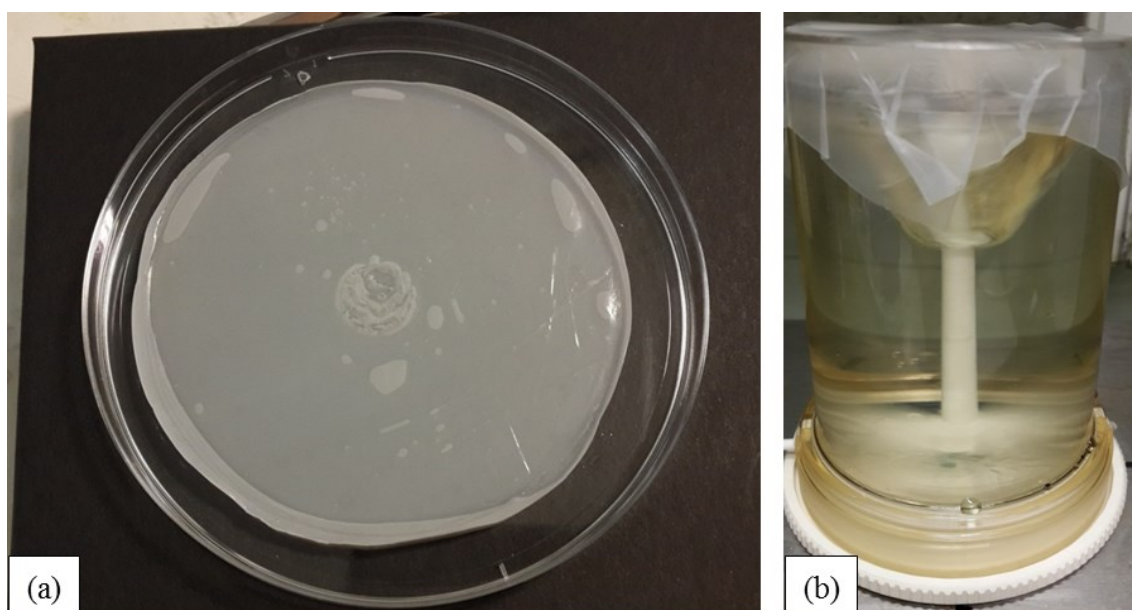


Figure 3.6 Photos of (a) Sample AT0 after running abrasion test for two days and (b) simulated abrasion test with low concentration suspension

Apart from the standard mechanical test, abrasion tests using a stirring cell with abrasive SiC suspension were conducted in order to study the abrasion resistance of the membranes. After running the test for 48 hours, Sample AT10 was found almost unchanged with eyes, while Samples AT0 to AT7 had a similar abraded membrane centre and the rest of the membrane was nearly unchanged, as shown in Figure 3.6 (a). The uneven abrasion along the radius dimension was caused by the enrichment of SiC particles on the membrane centre due to the vortex flow of water and the gravity of the particles, as shown in Figure 3.6 (b). There are two different regions and thus two different regimes of abrasion. Figure 3.7 compares the cross section structure of the tested Sample AT0 and Sample AT10 at different positions including the membrane centre, 1 cm radius, 2 cm radius and 3 cm radius. It was found that there was no obvious difference in the cross section structure at various radii for Sample AT10 after the abrasion test. However, for Sample AT0, the skin layer and the finger-like voids were almost worn away at the membrane centre during the test, whereas the outer three sites had a similar structure to the untested membrane. The membrane thicknesses at all four sites of each sample were measured from the SEM images and those for Sample AT0 are depicted in Figure 3.8. It was found that the membrane thickness decreased from the position of 1cm radius to 3cm radius. This was because the linear velocity of the abrasive SiC particles increased along with the radius and membrane was more abraded at larger linear velocity. Other membrane samples (AT0.5 to AT7) showed similar trends in the membrane thickness from 1cm to 3cm

radius, but with less reduction of the thickness. The results demonstrate that by incorporating PGS in the polymer matrix, the reinforced PVDF membranes were less abraded in the abrasion test. In order to give a quantitative and reproducible comparison, the membrane abrasion rate of different membranes was represented by the reduction of membrane thickness at the membrane centre after the 48-hour test. The change of thickness at the membrane centre was chosen to represent the abrasion rate because it shows the most pronounced and consistent change after the test. As shown in Figure 3.9, generally, the reduction of membrane thickness decreases as the loading amount of PGS increases, which further confirms that abrasion resistance was improved by the addition of PGS. In particular, Sample AT10 was barely affected after the test with a thickness reduction of only 0.14 μm , showing a drastic improvement of the abrasion resistance compared with 23.76 μm of unreinforced Sample AT0 and 11.16 μm of Sample AT7, which indicates that the abrasion resistance of the membrane can be significantly improved when a certain amount of PGS is added to the PVDF membranes.

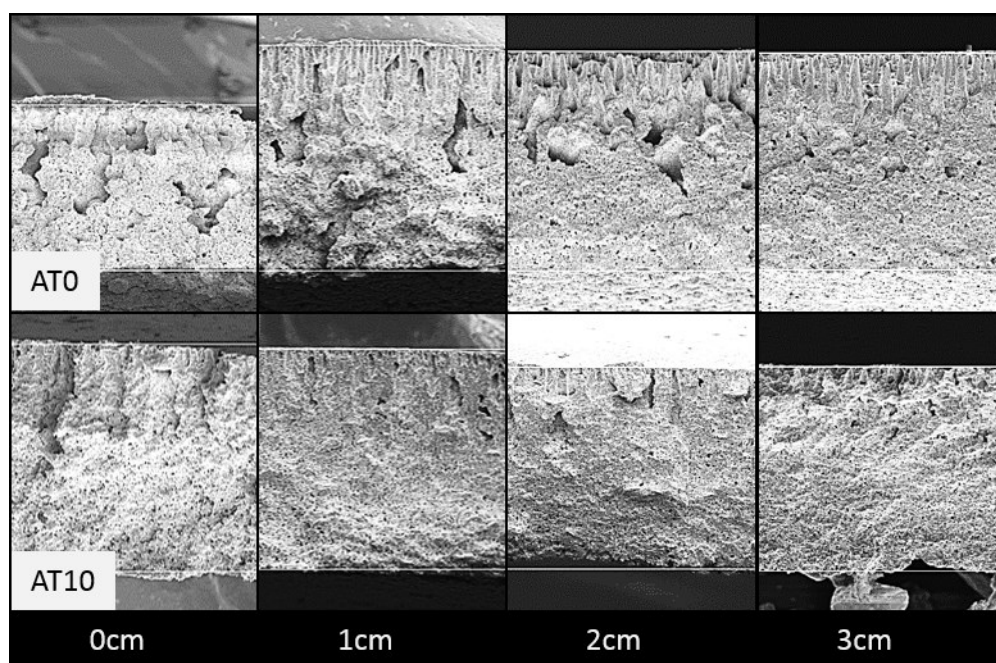


Figure 3.7 SEM images of the cross section structure of (top) Sample AT0 and (bottom) Sample AT10 at membrane centre, 1cm, 2cm and 3cm radius after the abrasion test (straight lines are used only to help locate the top and bottom edges of each membrane sample)

In terms of the abrasion behaviour, materials can be categorised as ductile or brittle materials according to the impingement angle of the maximum abrasion rate. Ductile materials, such as PVDF polymer, show the maximum abrasion at low impingement angles of around 30° , while brittle materials like the PGS filler, have the maximum abrasion rate at an impingement angle of 90° [32]. When the abrasive particle hits the material with an angle, the

impact force can be decomposed to two constituents: one is parallel and the other is vertical to the surface. In abrasion of ductile materials, the parallel force is dominant and the material is removed by microcutting and microploughing, thus the abrasion is more efficient at low impingement angles. In abrasion of brittle materials, the material is mainly damaged by microcracking due to vertical impact, and high impingement angles lead to more intensive abrasion. For composite materials, abrasion behaviour can vary between ductile and brittle depending on the material composition and the property of the filler [33-35]. In this study, as illustrated in Figure 3.9, the abrasion rate of the membrane samples except Sample AT4 was decreased by blending of PGS nanoclay in the PVDF matrix. And particularly, Sample AT10 showed a drastic reduction of the abrasion rate, indicating there might be a transition of the abrasion mechanism between Sample AT7 and Sample AT10 from a ductile or semi-ductile fashion to a brittle fashion. In this abrasion test, the membrane surface was hit by the SiC particles at a very low angle due to the high rotating speed used. For Samples AT0 to AT7 being a ductile or semi-ductile material, this low impingement angle was advantageous for abrasion, and thus the centre of the membranes was significantly abraded. However, the addition of PGS increased the fraction of the brittle part on the surface, thus the abrasion rate decreased along with the PGS content. For Sample AT10, which could have been turned to brittle material due to the higher PGS content, the abrasion at low angles was very slow compared with that of ductile or semi-ductile materials, and consequently the abrasion rate dropped drastically. Sample AT4 had an abnormally high abrasion rate, which could be attributed to its larger surface pore size compared with other samples, as it has been found that the surface morphology of ductile materials has a great influence on abrasion resistance [36].

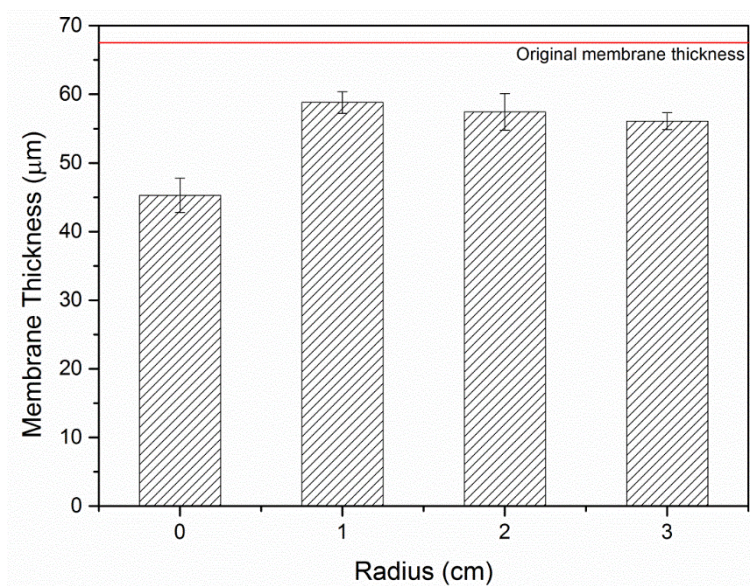


Figure 3.8 Membrane thickness of Sample AT0 at different positions after the abrasion test (red line is the original membrane thickness)

In this study, efforts were also made to find a possible correlation between the abrasion rate of the membrane samples and the mechanical properties including elongation ratio, tensile strength and Young's modulus. However, no clear correlation was established since membrane abrasion performance is mainly affected by the membrane surface properties while mechanical properties are decided by the entire membrane sample and may not be applied directly. Furthermore, hardness is one of the most concerned mechanical properties related to the abrasion resistance of materials. It is known that PGS nanoclay is more rigid than the PVDF polymer and hence the membrane hardness is supposed to increase with PGS loading. However, it was impossible to conduct the hardness test in this study due to the fact that the membrane samples were too thin and porous, which make a clear quantitative correlation between abrasion resistance and the mechanical properties even more difficult to establish for porous membranes.

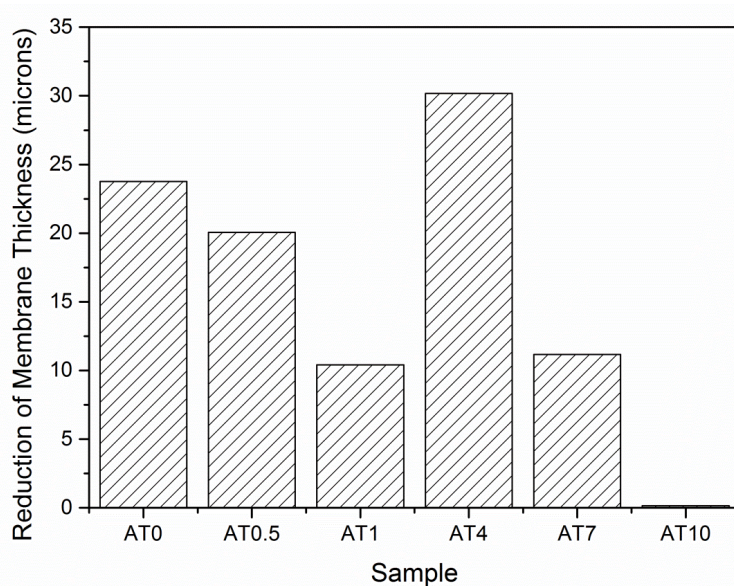


Figure 3.9 The reduction of membrane thickness of Samples AT0 - AT10 after the abrasion test

3.5 Conclusions

PGS nanoclay reinforced PVDF ultrafiltration membranes were prepared by a combination of immersion precipitation and thermally induced phase separation. The presence of PGS nanoclay in the PVDF polymer solution played a role as nucleation agent during the phase inversion process. As a result, the membrane structure composed of more PVDF crystallites with smaller size was observed as the loading of PGS nanoclay increased.

Furthermore, the incorporation of PGS nanoclay led to a considerable increase in the water permeability of the reinforced PVDF membranes. The tensile strength and Young's modulus of the reinforced membranes were also enhanced whereas elongation ratio was decreased. The PGS reinforced PVDF membranes were characterised by a specially designed abrasion test. The results showed that the reinforced membranes were less abraded and a drastic improvement of the abrasion resistance was found when the PGS loading amount reaches 10 wt.%.

However, in this study, the improvement of the permeation flux is not significant. And the enhancement of the abrasion resistance involves the use of extra chemical, which will increase the production cost and is unfavourable. Like most other modification techniques based on the phase inversion method, the study in this chapter is still an incremental improvement or refinement to PVDF membranes. A technological limit of the phase inversion approach has been therefore reached and there is an urgent need of developing new membrane manufacturing procedures.

3.6 References

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Chapter 4 Formation of Porous PVDF Membranes via the Combined Solvent Crystallisation and Polymer Diffusion Technique

4.1 Abstract

Currently, the production of porous polymeric membranes for filtration is predominated by the phase separation technique, which has been developed since the 1960s and has been widely employed as a standard manufacturing procedure for most polymeric membranes. However, a technological limit has been reached. And there has been no significant breakthrough over the last decade in terms of new manufacturing procedures, which produce membranes with high performances in an environmentally sustainable way. In this research, using poly(vinylidene fluoride) (PVDF, $-(\text{CH}_2\text{CF}_2)_n$) as a sample polymer, we propose a new concept of membrane manufacturing techniques by combining oriented green solvent crystallization and polymer migration. Unique asymmetric membranes with gradually opened micro-channels have been obtained. In the filtration test, the prepared membranes showed excellent performance with the pure water permeation flux 100 times higher than those with similar pore size prepared by conventional phase inversion processes. Compared to conventional membrane preparation processes, the new manufacturing procedure is governed by fewer operating parameters and is, thus, easier to control with reproducible results. These findings demonstrate the promise of a new concept for green manufacturing nanostructured polymeric membranes with high performances.

4.2 Introduction

Filtration is a separation process based on size exclusion through a porous media, where liquids and small particles pass the pores, but bigger particles are rejected. Porous membranes have been widely used in liquid filtration for drinking water production, wastewater treatment, dialysis, beverage clarification, etc. Membrane-based filtration is now a business of tens of billions USD per year, among which microfiltration (MF, pore size > 100 nm) and ultrafiltration (UF, pore size ranging from 2 to 100 nm) share the biggest part of the total membrane market.

Among all types of MF/UF membrane materials, PVDF is one of the most commonly used because of its outstanding properties, such as inertness in a wide range of harsh chemical

and thermal conditions, particularly surviving from chlorination disinfection with excellent mechanical strength in working conditions [1, 2]. All these excellent properties make PVDF membranes predominant in the pre-treatment units of seawater desalination and in wastewater treatment. However, PVDF membranes suffer from low permeation flux, and most commercial PVDF UF membranes for industrial use only possess pure water permeation flux of less than 200 litre per square meter per hour under 1 bar pressure difference (LMH bar^{-1}) across the membrane. To compensate the low flux of PVDF membranes, larger membrane areas are required to treat a large volume of water. It is very often that in a seawater desalination plant, the pre-treatment unit is composed of hundreds of PVDF UF membrane module trains occupying a large footprint. And the total PVDF membrane area could exceed $200,000 \text{ m}^2$ for a desalination plant with a capacity of $100,000 \text{ m}^3/\text{day}$. The requirement of large membrane area increases not only the capital investment, but also the daily operating costs (for energy and maintenance) of the filtration units. Improving the permeation flux of the PVDF membranes is therefore crucial to reduce the costs and energy consumption in the filtration plants.

Currently, PVDF membranes as well as other MF/UF polymeric membranes are produced via phase separation methods, predominately the non-solvent induced phase separation (NIPS) method [2, 3], although some commercial membranes are also produced by the thermally induced phase separation (TIPS) method [4-6]. An excellent review on the preparation and modification of PVDF membranes has been provided by Liu et al. [2]. Complex physical-chemical factors are involved in the NIPS process, such as inter-diffusion of solvent and non-solvent, rheology of polymer solution, interfacial instabilities, and even ambient temperature and humidity [2, 3, 7]. Thus, controlling the quality of final membrane products is extremely complicated, and often an ideal structure with minimised permeation resistance is difficult to achieve.

In the production of porous materials, a simple approach of “freeze-drying” is often used [8-10]. This method utilises randomly oriented solvent crystallites as template to produce flow passages (or pores) of micron-scale size in porous materials, where the separation takes place normally via adsorption rather than size exclusion. A few attempts have been made to produce membranes via this approach. For example, based on TIPS technique, Su et al. developed a freeze-gelation method, in which the PVDF films cast with various dope concentrations were placed in a refrigerator at $-10 \text{ }^\circ\text{C}$ for 2 h before being immersed in water for solvent exchange [11]. On the other hand, Kim and Lee prepared PVDF membranes with

pores of low tortuosity and high porosity by directional crystallisation of dimethyl sulfoxide (DMSO) [12]. The directional crystallisation was achieved under the temperature gradient provided by the controlled movement of the PVDF film towards the liquid nitrogen reservoir. After removing the solvent crystals, pores of low tortuosity and high porosity were formed in the obtained membranes. However, due to the lack of effective control of the size and orientation of the solvent crystallites, those attempts failed to produce membranes with pore sizes smaller than 250 nm, which is no difference compared to the flow passage of porous materials prepared by the same technique. Nevertheless, the freeze drying method seems to show great potential as a new concept of membrane production techniques.

4.3 Theory

In a typical freeze-drying process, a liquid sample is first frozen by contacting with or immersing in a cold bath. Then the frozen solvent inside the sample is removed by sublimation under vacuum, while the sample remains frozen at a temperature below its glass transition temperature or melting point [13, 14]. Thus, the porous structure of the obtained sample is formed by the space occupied by solvent crystallisation, and the solvent crystallites behave as pore-forming templates. Apparently, the freezing process is crucial to producing samples with desirable porous structures.

In the freezing process, solvent crystallises while the solute is excluded from the solvent crystals due to the low solubility of impurities in crystals, which leads to increased solute concentration in front of the solvent crystals [15]. As a result, a supercooling zone is formed and the solvent crystals grow by breaking down the planar interface [16-18]. The crystallisation of solvent molecules and thus the ultimate porous structure of the produced material can be affected by different freezing conditions, such as freezing temperature, freezing direction, solution concentration and nature of solvent and solute. For example, the mean pore size could be reduced by increasing the solution concentration or reducing the freezing temperature while maintaining other freezing parameters unchanged [19, 20].

In particular, the pore morphology is significantly affected by the freezing direction. Ordered porous structure can be achieved by orientating the growth of solvent crystals in one direction, which is called directional freezing [21] or unidirectional freezing [22]. In the unidirectional freezing process, a temperature gradient is applied by moving the sample towards the freezing bath at a controlled rate or simply contacting one side of the sample with the cooling source. As shown in Figure 4.1, solvent crystals grow from the bottom to the top

as the temperature increases, while solutes are expelled and solidify around the solvent crystals. Subsequently, aligned porous structure will be obtained after removal of the orientated solvent crystals. In some cases [9, 10], bridges between crystals may be formed due to the solutes trapped within the growing solvent crystals.

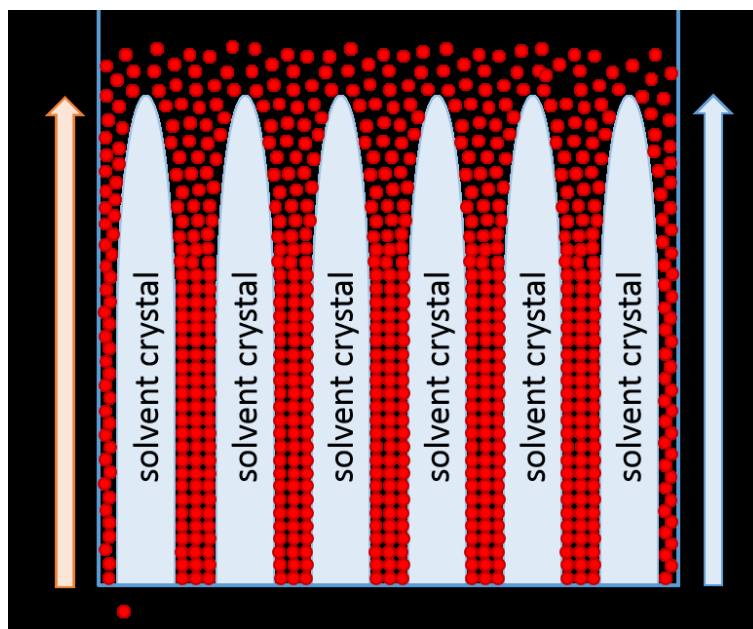


Figure 4.1 Schematic of unidirectional freezing process (adapted from [21])

In the practice of the freeze-drying approach, the actual nuclei/crystallite sizes obtained are determined by the kinetics of nucleation/crystallisation during the transient cooling stage [23]. The size and size distribution of the crystallites are dramatically affected by the cooling rate. With a fast cooling rate, the size would be small and the size distribution would be narrow, and vice versa [23]. On the other hand, during the late stage of crystallisation, small individual crystallites will agglomerate to form big grains due to the coarsening process. To achieve small crystallites and thus small pores in the final membranes, it is important not only to get small crystallites at the first place, but also to constrain the further growth of small individual crystallites during the late stage, especially to prohibit their agglomeration. The second challenge is much more difficult to tackle, and to the best of our knowledge, it has not been worked out by other researchers. Here we propose, by using a selected solvent and applying controlled unidirectional cooling, it is possible to create a chemical potential difference that drives the polymer solute to diffuse towards the cooled region. Then the growth of the solvent crystallites can be sterically hindered by the enriched polymer content, and a highly oriented pore structure can therefore be achieved.

4.4 Methodology

4.4.1 Materials

Commercial PVDF (Kynar[®] K-761, Mw = 440,000 Da, $\rho = 1.79 \text{ g/cm}^3$) was purchased from Elf Atochem and was dried at 80 °C for 24 hours before use. DMSO, *N,N*-dimethylacetamide (DMAc), *N*-Methyl-2-pyrrolidone (NMP), ethanol and hexane were purchased from Sigma-Aldrich, UK and were used as received.

4.4.2 Membrane Preparation

PVDF flat sheet membranes with highly asymmetric and self-assembled ordered structure were produced by a combined solvent crystallisation and polymer diffusion (CCD) method. The PVDF dope solutions were prepared by dissolving PVDF powder (20 wt.%) in DMSO at 80 °C or in NMP and DMAc at room temperature, and then was left in the oven at 80 °C overnight to remove bubbles. The dope solution was then cast of a certain thickness on a casting plate, followed by unidirectional cooling to a pre-determined temperature in two ways.

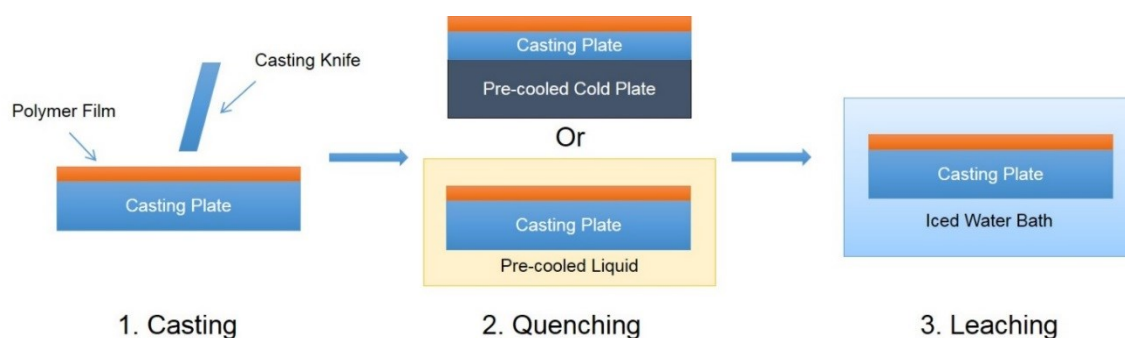


Figure 4.2 Schematic of the membrane preparation processes

As shown in Figure 4.2, one was transferring the casting plate onto a pre-cooled cold plate (-30 °C) on a freezing board, and the other was immersing the casting plate into a pre-cooled liquid such as hexane (-15 °C) or liquid nitrogen (-196 °C). For the former cases, the materials of the cold and casting plates was aluminium or glass to realize different thermal conductions and thus different cooling rates; for the later cases, a 1 cm thick glass casting plate was used to ensure fast cooling from only one side of the polymer casting film. After complete quenching, the frozen casting film was immersed in iced water to leach the solvent out. The water was changed regularly to remove the residual solvent. Apart from the materials of the plates, the casting thickness was varied in order to investigate its effects on the membrane morphology and properties. The preparation conditions of each sample were summarized in Table 4.1.

Table 4.1 Casting conditions for the preparation of flat sheet membranes

	Sample	Solvent	Casting Thickness	Casting Plate	Cold plate/ Cooling Condition
CCD	G/G*	DMSO	1mm	6 mm Glass	6 mm Glass plate at -30 °C
	Al/G	DMSO	1mm	6 mm Al	6 mm Al plate at -30 °C
	Al/Al 1.0 mm	DMSO	1mm	6 mm Al	6 mm Al plate at -30 °C
	Al/Al 0.5 mm	DMSO	0.5mm	6 mm Al	6 mm Al plate at -30 °C
	Al/Al 0.3 mm	DMSO	0.3mm	6 mm Al	6 mm Al plate at -30 °C
	Al/Al 0.1 mm	DMSO	0.1mm	6 mm Al	6 mm Al plate at -30 °C
	Hexane	DMSO	1mm	10 mm Glass	Hexane bath at -15 °C
	Liquid Nitrogen	DMSO	1mm	10 mm Glass	Liquid nitrogen (-196 °C)
	Al/Al NMP	NMP	1 mm	6 mm Al	6 mm Al plate at -30 °C
	Al/Al DMAc	DMAc	1 mm	6 mm Al	6 mm Al plate at -30 °C

*: material of the casting plate/material of the cooling plate, G represents glass and Al stands for aluminum.

4.4.3 Membrane Characterisation

The wet membranes were used directly for filtration tests and gas-liquid displacement porosimetry, but were dried via solvent (ethanol) exchange technique prior to SEM and mercury intrusion porosimetry.

The morphology of each membrane sample including separation layer, supporting layer and cross section was observed by scanning electron microscope (SEM), as described in Section 3.3.3.1.

4.4.3.1 Pure Water Permeation Test

In order to evaluate the membrane permeability, pure water permeation tests were conducted using a 300 mL dead-end filtration cell (HP4750 Stirred Cell, Sterlitech Corporation, USA). The PVDF membrane samples prepared by the CCD method were tested directly at 1 bar without any pre-treatment such as membrane compaction at higher pressure. This is because the membrane samples prepared by such a method possessed excellent mechanical strength and could withstand high pressure without any flux decline being observed. The permeance of the membrane was calculated based on the equation shown below:

Equation 4.1
$$J = \frac{V}{A \times t}$$

where J is the water flux, V is the permeate volume, A is the effective membrane area, t is the time of permeate collection.

4.4.3.2 Gas-Liquid Displacement Porosimetry

In this work, the membrane pore size and pore size distribution were characterized by the gas-liquid displacement method using POROLUX 1000 (POROMETER nv, Belgium). The wet membrane was cut into certain sizes and was wetted with a specific wetting liquid, POREFIL™ (POROMETER nv, Belgium). In each measurement, the pressure of the testing gas N₂ was increased from 0 to 34.5 bar step by step to replace the wetting liquid inside the membrane pores. At each step, both the pressure and the flow had to be stabilized within $\pm 1\%$ for 2 s before the data was recorded. The relevant pore size corresponding to each operating pressure can be calculated based on the Young-Laplace equation:

Equation 4.2
$$d = \frac{4\gamma \cos \theta}{\Delta P}$$

where d is the diameter of the pores behaving as gas paths and contributing to the gas flow at each operating pressure; γ is the surface tension of the wetting liquid, which is 16 mN/m; θ is the contact angle of the wetting liquid on the membrane surface, which is 0°; ΔP is the specific operating pressure.

It should be noted that only the neck size of open pores could be measured using this method. For each sample, the mean flow pore (MFP) diameter and pore size flow distribution were obtained.

4.4.3.3 Mercury Intrusion Porosimetry

For two typical CCD membrane samples, Al/Al 1.0mm and Al/G 1.0mm, mercury intrusion data were also collected at absolute pressure ranging between 1.38×10^3 and 2.28×10^8 Pa (0.2 – 33500 psi) (Micromeritics Autopore IV) with an equilibration time of 10 s and assuming a mercury contact angle of 130°. The flat sheet membranes were cut into sections of approximately 4 mm in diameter prior to the mercury intrusion analysis.

4.4.4 Calculation of Temperature Profiles and Cooling Rates

Transient temperature profiles across the polymer casting films and the cooling rates at fixed positions in the casting film were calculated by the commonly used finite difference method with the explicit scheme [24]. The 1D heat conduction models for the scenarios involved in this research were set as below.

4.4.4.1 Cooling with a Pre-Cooled Cold Plate

The setting of the initial conditions for the calculation of thermal conduction and temperature profiles under the circumstance of cooling with a pre-cooled cold plate is illustrated in Figure 4.3.

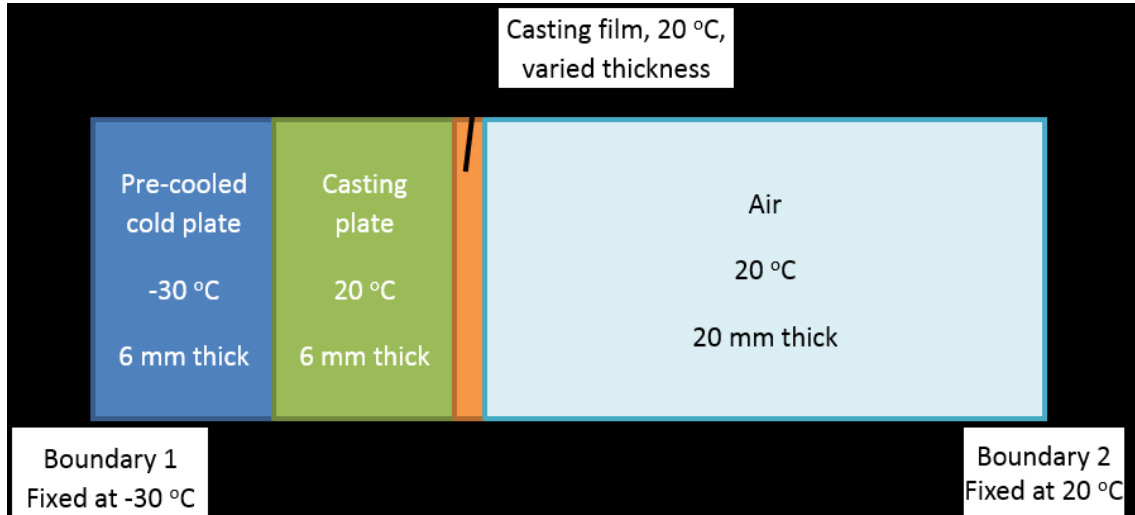


Figure 4.3 The setting of initial conditions for the calculation of thermal conduction under the circumstance of unidirectional cooling with a pre-cooled cold plate

The boundary of the cold plate was fixed at -30 °C, as it was continuously cooled by a freezer. A 20 mm air gap was used to allow the temperature of the top surface of the polymer casting film to change, and the boundary was fixed at 20 °C. The thickness of the air gap has a little influence on the final temperature of the top surface of the polymer film, but basically produces no difference within the time of interest.

Heat conduction in the layers of different materials was deemed as heat diffusion along 1D grids, on which points with an interval (Δx) of 5 μm were used to solve the heat conduction equation numerically:

Equation 4.3
$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2}$$

where T is the temperature, t is the time, x is the distance and κ is the thermal diffusivity. The thermal diffusivity κ is defined as

Equation 4.4
$$\kappa = \frac{k}{\rho c_p}$$

where ρ is density, c_p is heat capacity and k is thermal conductivity.

Inside each homogeneous material layer, heat conduction is calculated by

Equation 4.5

$$T_i^{n+1} = T_i^n + \kappa \Delta t \left(\frac{T_{i+1}^n - 2T_i^n + T_{i-1}^n}{(\Delta x)^2} \right)$$

and at the interface between different material layers, heat conduction is calculated by

Equation 4.6

$$T_i^{n+1} = T_i^n + \frac{\kappa_{i-1} \Delta t}{(\Delta x)^2} T_{i-1}^n - \left(\frac{\kappa_{i-1} \Delta t}{(\Delta x)^2} + \frac{\kappa_i \Delta t}{(\Delta x)^2} \right) T_i^n + \frac{\kappa_i \Delta t}{(\Delta x)^2} T_{i+1}^n$$

where i is the position on the grid, and n is the number of the time step Δt , which is set $2\kappa\Delta t \leq (\Delta x)^2$ to meet the criteria of stability for the calculation.

4.4.4.2 Cooling by Immersing into Liquid Nitrogen or Pre-Cooled Hexane

In these two cases, the same algorithm was used, but the grids and boundary conditions were different, as shown in Figure 4.4.

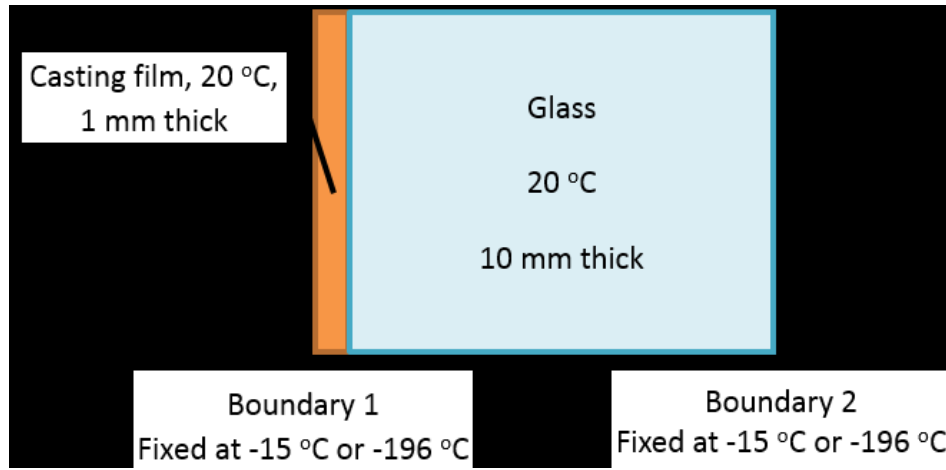


Figure 4.4 The setting of initial conditions for the calculation of thermal conduction under the circumstance of unidirectional cooling with a pre-cooled liquid

To simplify the calculation and to keep the calculating time within a manageable duration, and also due to the lack of available literatures, it is assumed that the thermal diffusivities in all layers are constant within the temperature range of interest, and it does not change in the casting film even if the film is turned from liquid to solid. This will of course cause some inaccuracy but will not alter the trends shown in the results. That is because within such a relatively short temperature range for calculation (from 20 °C to -30 °C, except the case of liquid nitrogen, in which the lower temperature ranging from -30 °C to -196 °C is no longer interested), the change in the thermal diffusivity is usually very small. And for common solvents and polymers, the thermal diffusivity usually does not change significantly when phase transformation happens. The thickness change of the casting film during the cooling process was also not taken into account, since the change was small and should not lead significant effects to the temperature profiles.

4.5 Results and Discussions

4.5.1 Proposed Mechanism

In the CCD process with a selected solvent whose melting point is slightly lower than the room temperature, when a casting polymer solution is unidirectionally cooled from one side to a temperature well below the freezing point of the solvent, a temperature gradient would be built in the casting film. The mechanism of membrane formation could be explained as follows using cooling from the casting plate as an example, as shown in Figure 4.5.

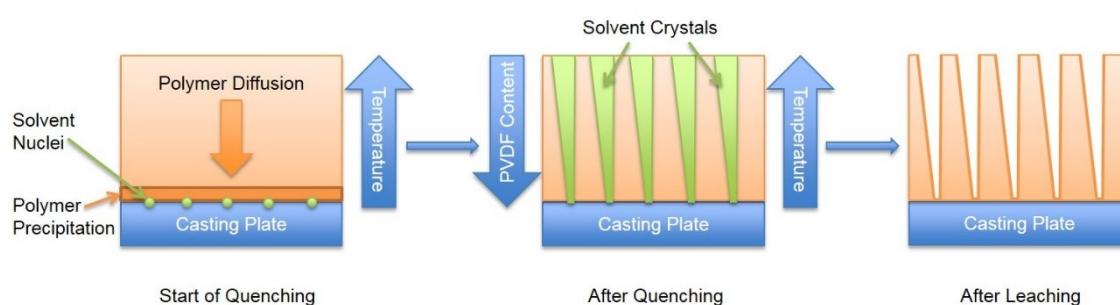


Figure 4.5 Schematic of proposed mechanism of the CCD method

At the colder side, accompanying with the nucleation/crystallisation of the solvent, the remaining polymer solution would enter the unstable region in the phase diagram and start to demix due to both the loss of the solvent in the liquid phase and the decreased solubility of the polymer at lower temperatures. Upon demixing/phase separation, the polymer starts to precipitate instantly, which leads the polymer concentration in the remaining liquid phase to be much smaller than the adjacent polymer solution at higher temperatures. Then the polymer solute is driven to diffuse towards the cold end, forming a denser layer than the warmer parts. It is apparent that the amount of the diffused polymer solute is determined by the diffusivity of the polymer and the polymer concentration difference, which is affected by the temperature gradient and the time available for diffusion before the liquid phase is frozen. In an ideal condition, enough polymer solute can diffuse to the cold end accompanying with the nucleation/crystallisation of the solvent, and fill the space between solvent crystallites, thus sterically hindering the agglomeration of the crystallites to remain their small size.

On the other hand, at the warmer part, solvent crystals would agglomerate and the size of the big grain would increase due to the decreased polymer concentration and hence less steric resistance. As a result, after removing the solvent crystals, the resultant membrane would have an asymmetric structure with a considerably porous dense separation layer and gradually opened channels, which have been commonly observed in the freeze-drying process when

unidirectional cooling is applied due to the Mullins–Sekerka instability [8, 25, 26]. Figure 4.6 shows clearly the structural features of a CCD Al/Al PVDF membrane prepared with 0.3 mm casting thickness. In this membrane, a thin separation layer is supported by numerous very well arranged micro-channels whose size gradually increases from the separation layer (Figure 4.6 (a)). The cross section image of the membrane shows clearly a number of tortuous pores in the separation layer, and intensively scattered pores on membrane surface (Figure 4.6 (b, c)). Furthermore, the supporting layer of the CCD membranes is composed of fully opened, oriented and interconnected micro-channels, which actually give negligible resistances to the water permeation (Figure 4.6 (d)).

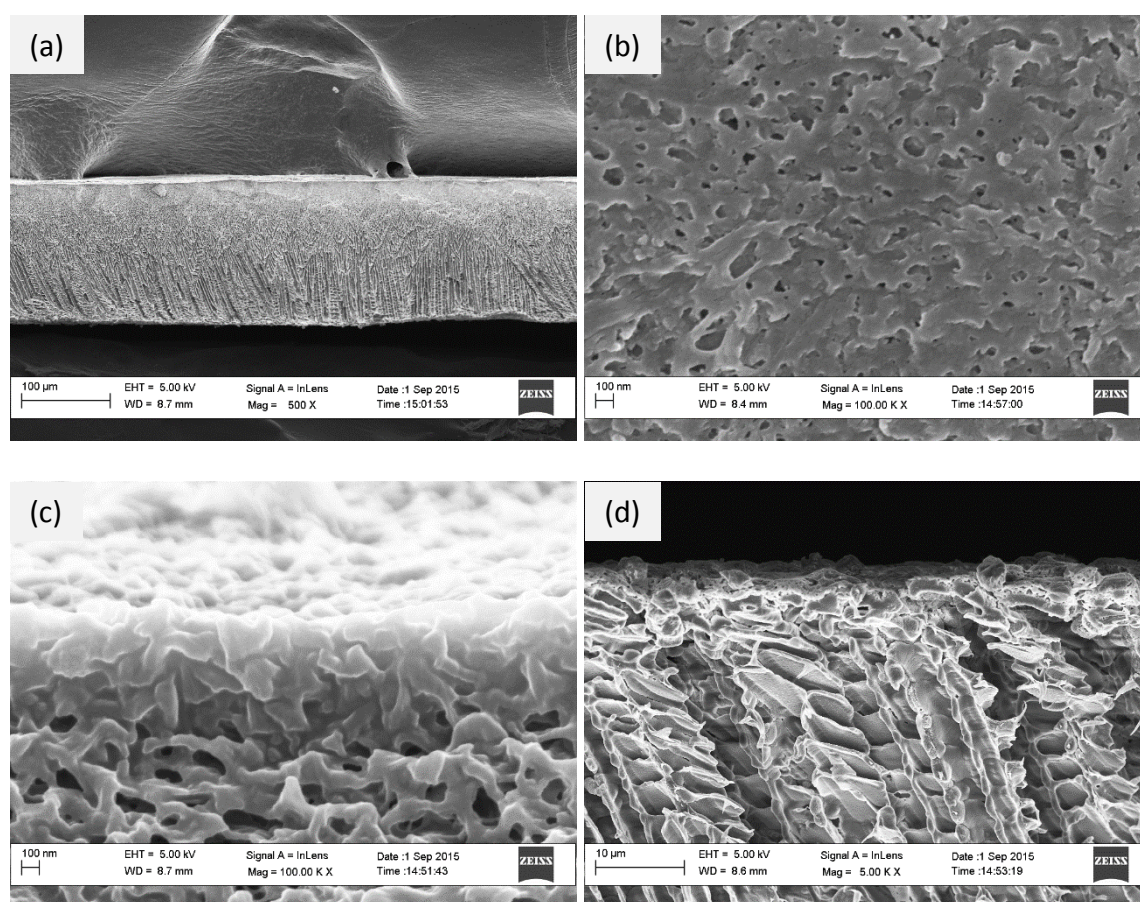


Figure 4.6 SEM images of the CCD Al/Al PVDF membrane prepared with a 0.3 mm casting thickness: (a) cross-sectional overview; (b) pores on the surface; (c) pore structure in the separation layer; (d) cross-sectional view of interconnected micro-channels at the back side

4.5.2 Effect of Cooling Conditions

Based on the proposed mechanism of the CCD process discussed in the previous section, it could be deduced that with a fast cooling rate, the crystal size at the cooler side would be smaller and thus, the pore size of the separation layer would be smaller and the pore size

distribution would be narrower, and vice versa. In this study, the effects of the cooling conditions on the membrane structure and performance were investigated by varying the quenching approaches, i.e. different combinations of the casting plate and cooling plate, and different pre-cooled liquids. In the former case, the plates are made of glass or aluminum with the same thickness, while in the latter case, pre-cooled hexane (-15 °C) and liquid nitrogen (-196 °C) were used.

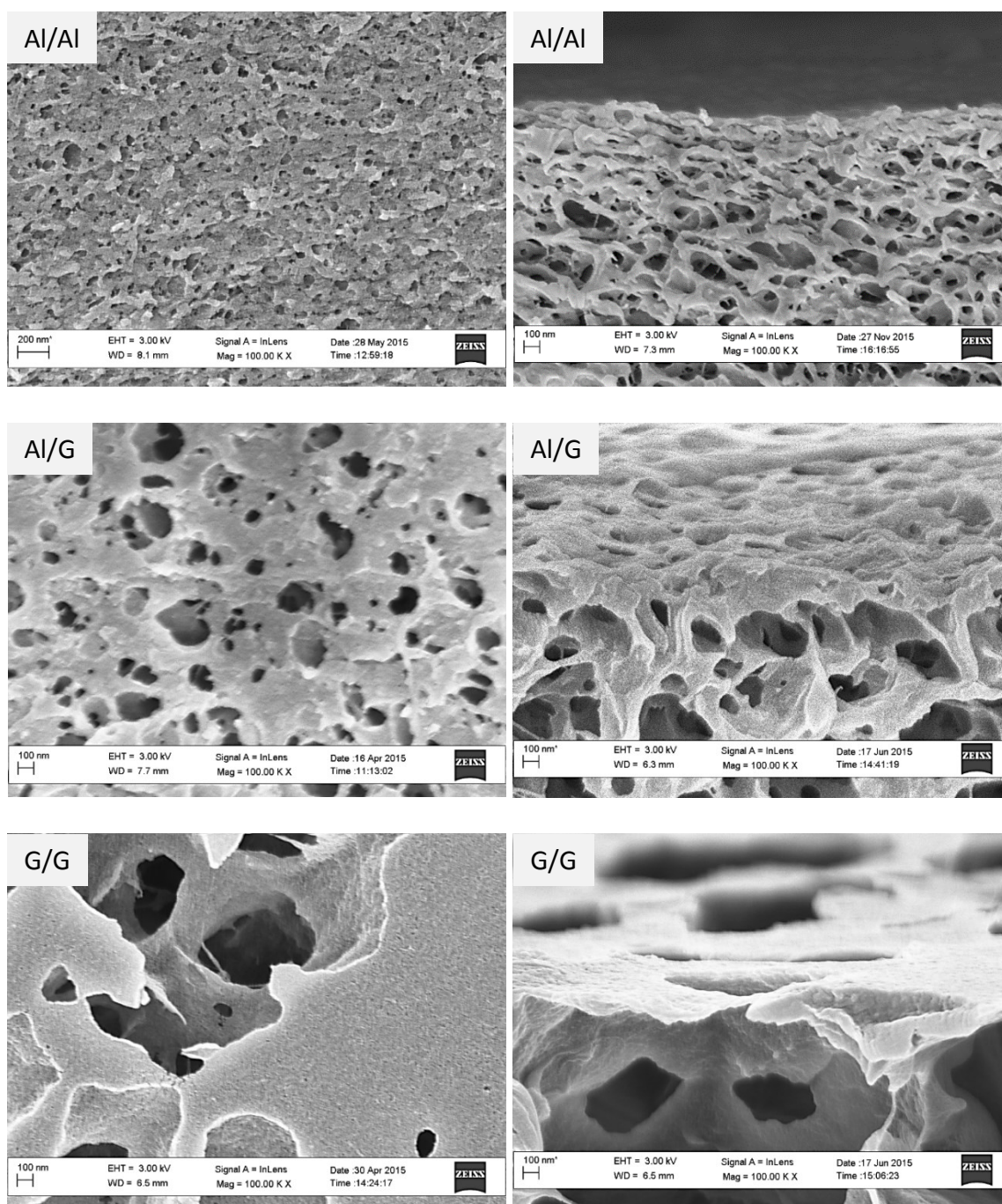


Figure 4.7 SEM images of (left) surface morphology and (right) close cross-sectional view of the separation layers of membranes prepared by using different combinations of casting plate

and cooling plate

Transient temperature profiles across the casting polymer films and the cooling rates at fixed positions in the casting film were calculated by the finite difference method using Matlab and the data were plotted in Figure 4.8. Apparently, in the case of Al/G and G/G samples, the slow cooling rates would have produced bigger initial DMSO crystals than the Al/Al sample. And the temperature gradients in the cold-end region are also much less steep than the latter case, which would have resulted in slower polymer diffusions. Both factors will contribute to the formation of bigger pore size in G/G and Al/G samples, as verified by the SEM images (see Figure 4.7). However, it is difficult to tell which factor is more important during the membrane formation process.

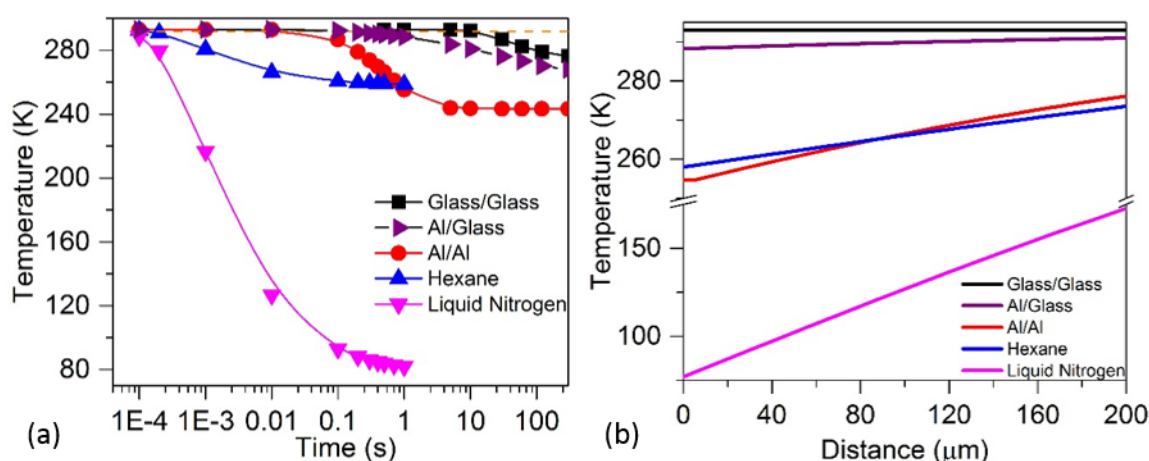


Figure 4.8 (a) the calculated temperature changes at the position of 10 μm from the cold-end interface of the polymer film; (b) the temperature profiles from the cold end of the cast films after cooling for 1 s

On the other hand, those cases using pre-cooled hexane and liquid nitrogen clearly show the importance of polymer diffusion. As shown in Figure 4.8 (a), when immersed into the pre-cooled hexane and liquid nitrogen, the polymer film underwent much faster cooling than the Al/Al case, and the initial DMSO crystallites in principle should be smaller than the Al/Al case. However, the pore sizes in both cases are even bigger than the G/G case, as shown in Figure 4.7 and Figure 4.9. In both cases, although a temperature gradient similar to or larger than the Al/Al case was applied (see Figure 4.8 (b)), the polymer film at the cold end (10 μm from the cooling interface, for example) was cooled down to less than 7 $^{\circ}\text{C}$ within 0.001 s. This means that the polymer film would be frozen almost instantly, leaving virtually no time for polymer to diffuse. As a consequence, the initial DMSO crystallites were allowed to agglomerate to form bigger grains resulting in big pores in the final membranes.

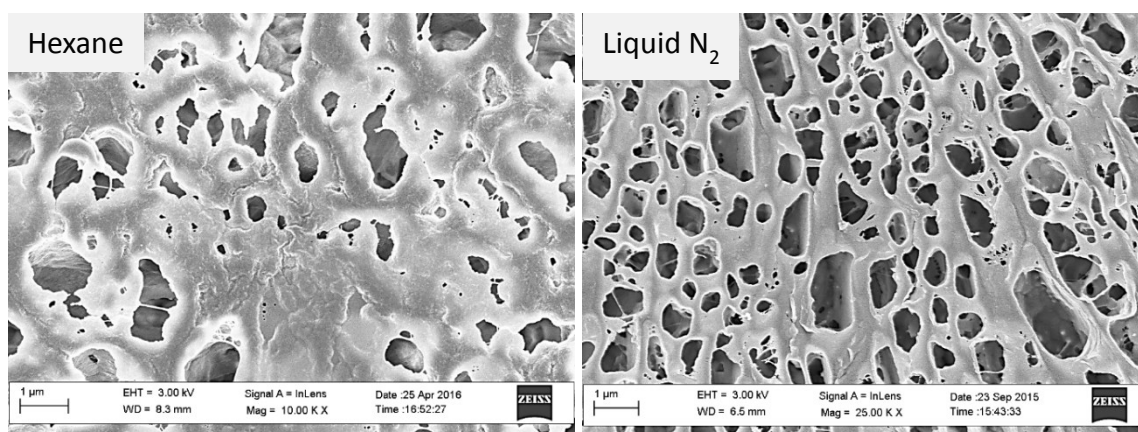


Figure 4.9 SEM images of the surface morphologies of CCD membranes prepared with (left) pre-cooled hexane and (right) liquid nitrogen

Generally, membranes prepared by the CCD method have an asymmetric structure with a porous surface layer supported by gradually opened micro-channels. Such structure could dramatically reduce the membrane resistance and the CCD membrane did show excellent performance in the filtration test. Table 4.2 summarises the permeation characteristics of these CCD membranes and compares with some commercial PVDF membranes. For the MF CCD membranes with pore sizes of 119 nm and 345 nm, the pure water flux reached stunning 5017 and 10998 LMH bar⁻¹, respectively. And for the UF membranes, it shows that the pure water permeation flux of the CCD membranes is substantially higher than the commercial membranes. The CCD Al/Al membranes showed pure water flux of up to 861 LMH bar⁻¹, which are one order of magnitude higher than the commercial membranes with similar pore size.

Table 4.2 Permeation characteristics of CCD PVDF membranes and some commercial PVDF membranes

Membrane Samples	Pure Water Flux (LMH bar ⁻¹)	Mean Flow Pore Size (nm)
G/G 1.0mm*	10998 ± 407	345 ± 26
Al/G 1.0mm	5017 ± 547	119 ± 10
Al/Al 1.0mm	861 ± 78	45 ± 3
Al/Al 0.5mm	570 ± 37	29 ± 3
Al/Al 0.3mm	608 ± 82	30 ± 9
Al/Al 0.1mm	486 ± 28	38 ± 11
Hexane	14062 ± 638	948 ± 119
Liquid Nitrogen	--	--
DOW**	40-120	30

EVOQUA	20	40
KOCH PURON®	100	30
GE ZeeWeed 1500	135	20
TORAY	30 (MBR conditions)	80
Pall	>3000	200
Pall	>8200	450
TriSep TM10	90	200
Hydranautics HYDRAcap®	34-110	80

*: Sample names are ended with casting thickness.

**: Pore sizes are nominal pore sizes provided by the manufacturers, whereas water flux is converted from product brochures of the membrane modules, but operation pressure and other conditions are unclear.

As illustrated in Figure 4.10 (a), the mercury intrusion results of the Al/Al and Al/G membranes show typical cumulative intrusion volume-pore size curves similar to those rigid pore structures such as in ceramic membranes, with an overall porosity of about 75-76 % and a broad pore size distribution from around 20 μm to less than 0.1 μm . The gradually increased intrusion volume reflects the gradual change in the pore size from the backside to the bottom separation layer in the CCD membranes. As expected, the incremental intrusion data (Figure 4.10 (b)) of the Al/Al membrane reveals a smaller pore size (11 μm) than the Al/G membrane (17 μm) at which intrusion starts, which correspond to the openings of the micro-channels on the backside. The average pore size of the Al/Al membrane is also smaller than the Al/G membrane. Closer observation of the incremental intrusion results (Figure 4.10 (c)) shows that the Al/Al membrane has higher pore volume at the pore size range of less than 100 nm than the Al/G membrane. These results agree very well with SEM images and gas-liquid displacement porosimetry results, and also agree with the prediction of membrane structure based on the cooling rate.

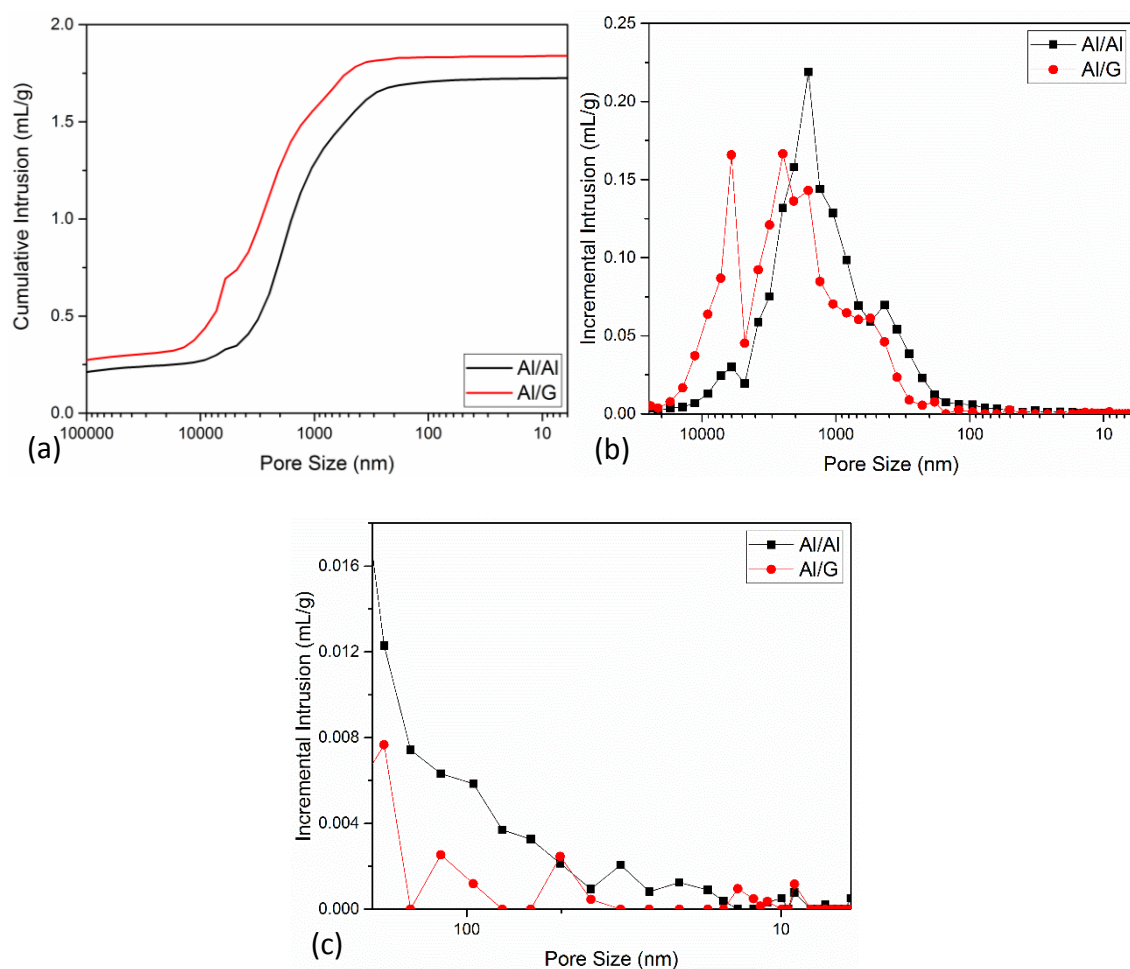


Figure 4.10 Mercury intrusion porosimetry results of CCD Al/G 1.0 mm membrane and Al/Al 1.0 mm membrane. (a) Cumulative intrusion volume vs. pore size; (b) incremental intrusion volume vs. pore size; (c) incremental intrusion volume vs. pore size within small pore size range

4.5.3 Effect of Casting Thickness

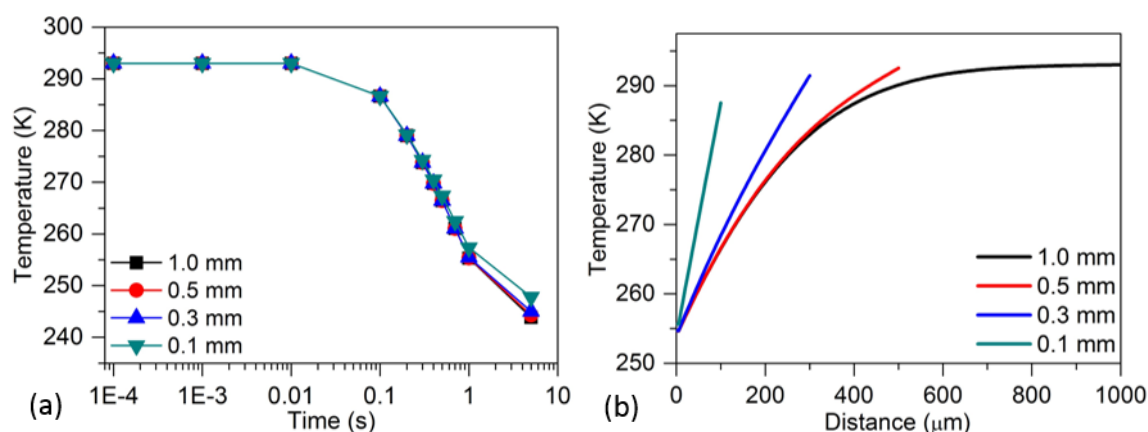


Figure 4.11 (a) the calculated temperature changes at the position of 10 μm from the cold-end interface of the polymer film; (b) the temperature profiles from the cold end of the cast films after cooling for 1 s

The effect of varied casting thickness on the membrane structure and performance were also studied in this work. As depicted in Table 4.2, a very interesting correlation between the permeation flux and membrane thickness was found, i.e. the flux increases as the thickness increases. It can be seen that the pore size did not show significant changes as varying the thickness, but the flux increased from 486 LMH bar⁻¹ for the 100 μ m thick membrane gradually to 861 LMH bar⁻¹ for the 1 mm thick membrane. This trend can be attributed to different PVDF diffusion rates during the unidirectional cooling. It can be calculated that by changing the thickness of casting film, the cooling rate at the cold end was almost not affected during the time of interest (Figure 4.11 (a)). However, the temperature gradient increases when the thickness reduces (Figure 4.11 (b)), which would provide a larger driving force for the polymer solute to diffuse to the cold end and thus form a denser and thicker separation layer, and thus smaller permeation flux. The changes in the thickness and the density of the separation layer are clearly revealed by SEM images (Figure 4.12), which agree very well with the trends of the pure water flux and the temperature gradient.

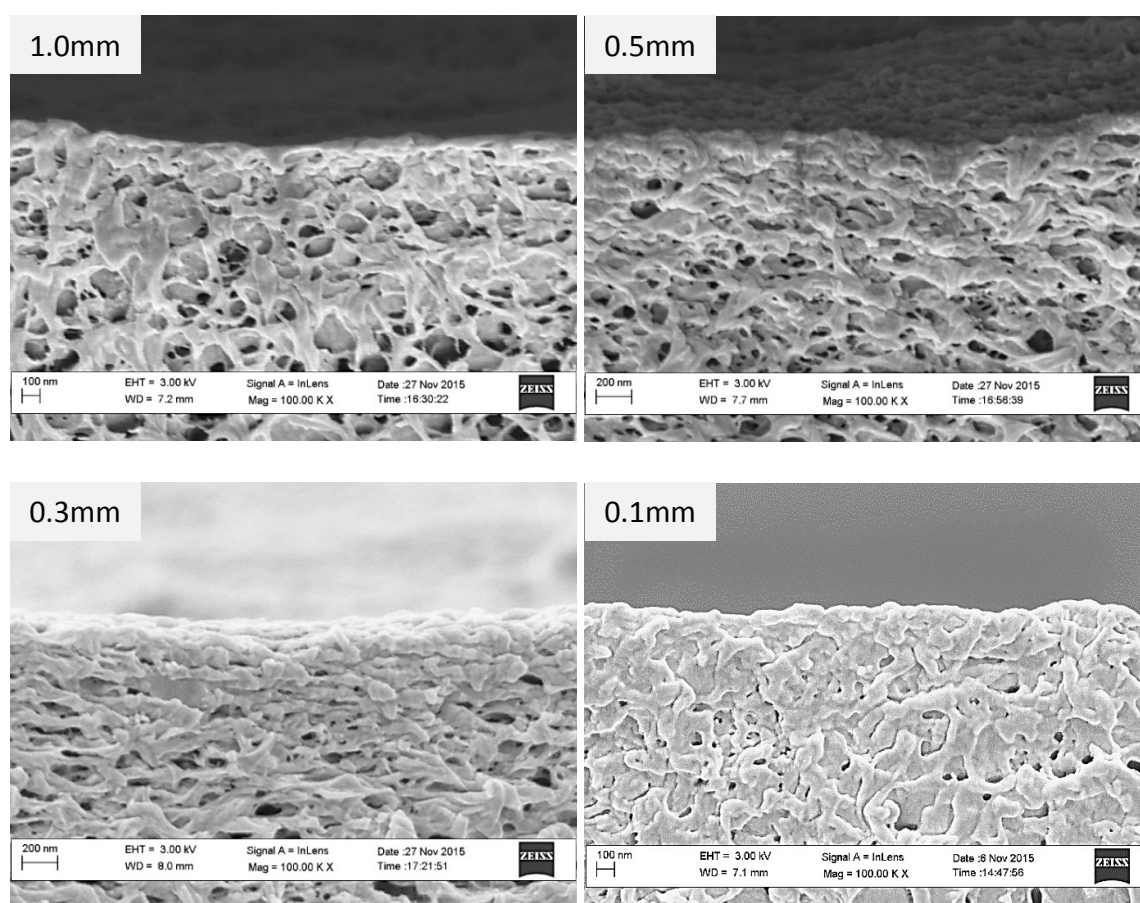


Figure 4.12 Close cross-sectional view of the separation layers of CCD Al/Al PVDF membranes prepared with varied casting thickness

4.5.4 Effect of Solvent Nature

In the above cases, the 20 wt.% PVDF/DMSO solution has a high freezing point of 14.3 °C, which is lower than the melting point of pure DMSO due to the presence of polymer. And no phase separation of the solution was observed before freezing, which confirms early solvent crystallisation prior to the phase separation of the polymer solution. On the other hand, if the sequence of phase separation and solvent crystallisation was altered, the results would be totally different. In two other Al/Al cooling cases (-30 °C), we used NMP and DMAc as the solvent, whose melting points are considerably lower than room temperature (-24°C and -20°C, respectively). Thus, phase separation happens prior to the crystallisation of the solvent due to the reduction of solvent power. The reversed sequence of phase separation and solvent crystallisation in both polymer solution was confirmed experimentally, as phase separation was observed at 5 °C for the PVDF/DMAc solution and -24 °C for the PVDF/NMP solution. While the freezing point was -25 °C for the former, and lower than -28 °C for the later.

As shown in Figure 4.13, the NMP Al/Al membrane has a sponge-like structure in the supporting layer, and no micro-channels were formed. This is due to the low melting point at -24 °C, which is 46 °C lower than the room temperature. Within this large temperature difference, phase separation of the PVDF solution had happened long before the crystallisation of NMP, and the formed polymer blocks would prohibit the formation of micro-channels during later NMP crystallisation. However, polymer diffusion from the warmer part to the cold end still happens. Due to the longer available time for diffusion, the dense separation layer in the NMP Al/Al membrane reached 5 µm, which is much thicker than the DMSO Al/Al membrane. And since the formation of the separation layer was earlier than NMP crystallisation, no NMP crystallites presented in the separation layer and therefore, there were no nano-scale pores formed from NMP crystallites. This thick and dense separation layer showed a very low pure water flux of 6.5 LMH bar⁻¹, and no pores larger than 18.6 nm were detected with gas-liquid displacement porosimetry.

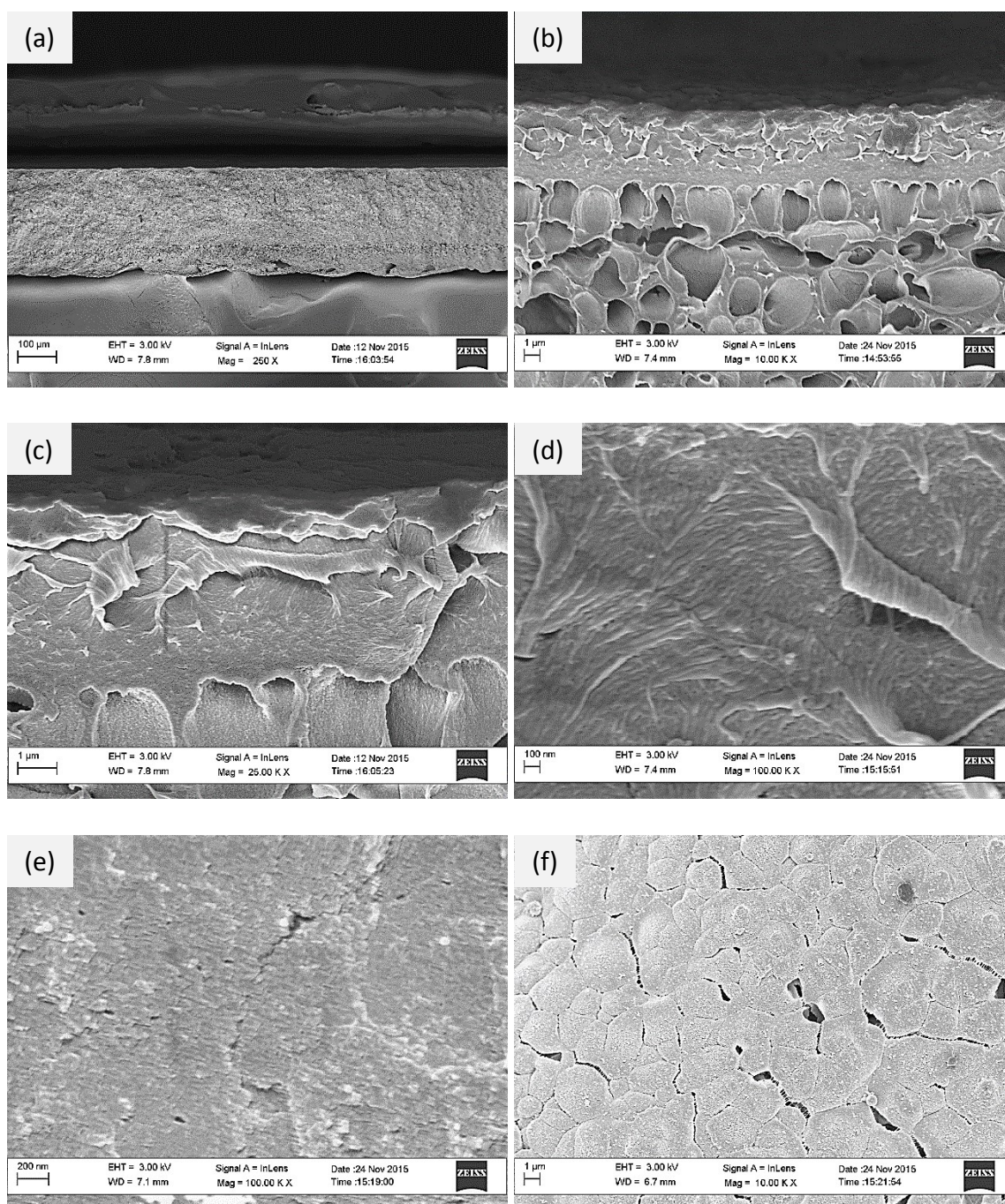


Figure 4.13 SEM images of the CCD Al/Al NMP PVDF membrane. (a) Cross-sectional overview; (b, c) close view showing the separation layer; (d) high-magnification image at the separation layer; (e) surface of the separation layer; (f) surface of the back side

Similar to the NMP case, the DMAc (melting point at $-20\text{ }^{\circ}\text{C}$) Al/Al membrane also shows a homogeneous but porous supporting layer and a dense top layer, as shown in Figure 4.14. However, this membrane broke apart when the crystallisation of DMAc was finished and only debris was obtained, which might be due to the damaging shape of DMAc crystal grains that cuts the membrane. The SEM images show some deep cracks formed at the air side of the

membrane. Permeation characteristics such as pore size and pure water flux are therefore not obtained for this membrane.

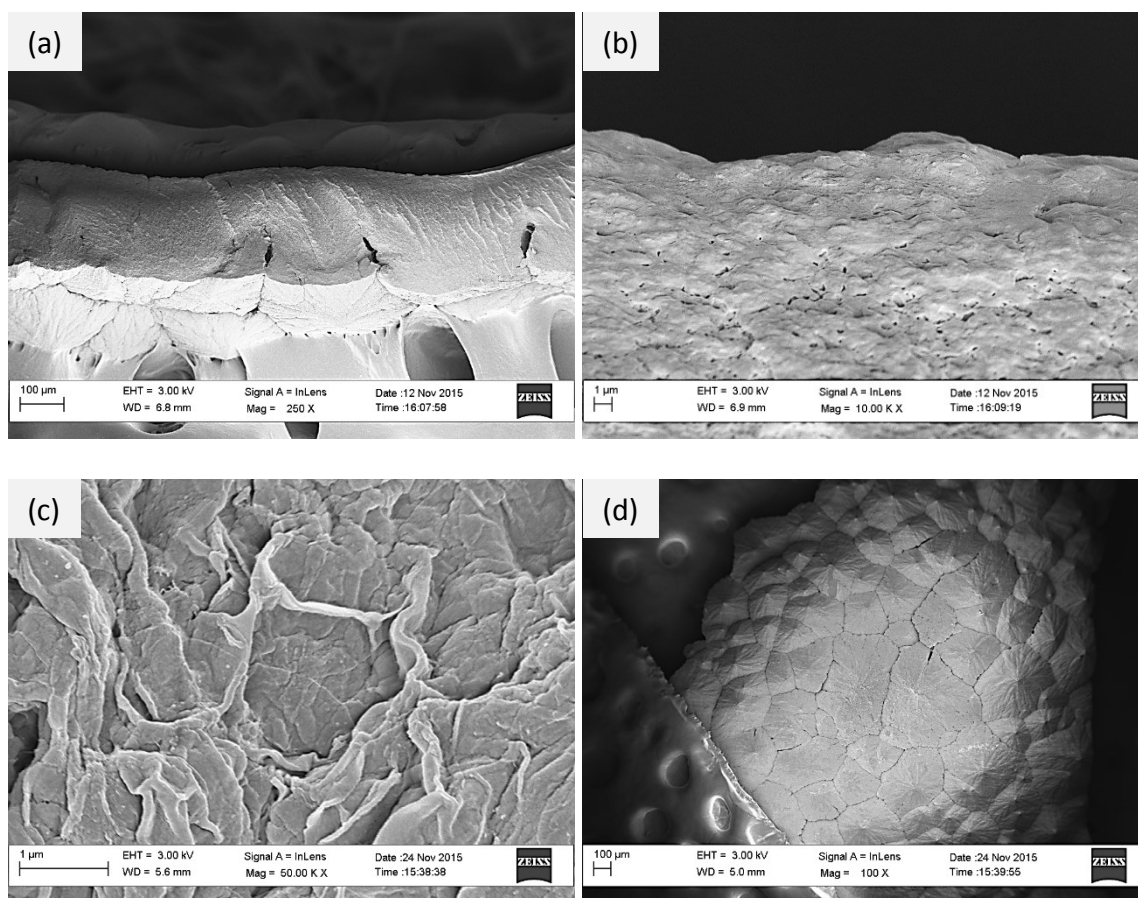


Figure 4.14 SEM images of the CCD Al/Al DMAc PVDF membrane. (A) Cross-sectional overview; (B) close view showing the separation layer; (C) surface of the separation layer; (D) surface of the back side

In both cases, due to the precipitated solid polymer blocks that led steric hindrance effect to lateral solvent crystallisation, the formation of micro-channels was prevented. Consequently, the membranes have a quite homogenous structure, which is commonly observed in membranes prepared via the TIPS method. And in both membranes, a thick and dense separation layer was formed at the cold side because of the low freezing points of NMP and DMAc, which gave prolonged time for PVDF solute to diffuse before solvent crystallisation. Since the dense separation layer was formed before solvent crystallisation, no solvent crystallites are expected to present in this layer. In fact, no visible pores were found in this layer under high-resolution SEM.

4.6 Conclusions

In summary, we have proposed a method through which the conventional freeze-drying approach can be adapted for membrane manufacturing. Membranes with effective pore sizes down to 30 nm were achieved in this study. The prepared membranes have a unique asymmetric structure composed of a porous dense separation layer supported by gradually opened micro-channels. The CCD membranes have also shown excellent permeation performance compared to commercial PVDF membranes, and they are of great potential to upgrade the existing filtration units. Other characterisations will be carried out in our future work including Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis on the phase structure of PVDF crystals, water contact angle measurement of the membrane surface hydrophilicity, fouling test, mechanical test and abrasion test. A comprehensive comparison between the CCD method and the NIPS method for flat sheet membrane production will also be made.

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Chapter 5 Permeation Characteristics and Mechanical Properties of the PVDF Membranes Prepared by the CCD Technique

5.1 Abstract

The production of polymeric microfiltration/ultrafiltration (MF/UF) membranes has been dominated by the phase inversion technique for decades. A technological limit has been reached in terms of the use of hazardous solvents in quantity and the relatively poor filtration capacity regarding the high demand. In Chapter 4, a new membrane preparation method has been developed by combining solvent crystallisation and polymer diffusion (CCD). In this work, poly(vinylidene fluoride) (PVDF) flat sheet membranes were produced by both the novel CCD method and the conventional non-solvent induced phase separation (NIPS) method. Comparisons between the CCD membranes and NIPS membranes were made based on the membrane structure, crystal phase, surface hydrophilicity, filtration performance, mechanical strength and abrasion resistance. The new CCD membranes have shown high permeation flux and excellent steady flux after fouling in the filtration test, and also displayed superior mechanical properties of high-pressure load and better abrasion resistance. All these outstanding properties enable the CCD membranes to replace the existing NIPS PVDF membrane modules in the filtration plants.

5.2 Introduction

Water shortage has become a global concern due to the increasing population and water pollution. Among the various techniques developed for water treatment, membrane separation has been widely applied in drinking water production and wastewater treatment. PVDF membranes have attracted much attention from researchers and industrial manufacturers for many years due to their excellent thermal and chemical resistance as well as high mechanical strength [1, 2]. PVDF MF/UF membranes have been therefore widely utilized in the applications of drinking water production, pre-treatment for reverse osmosis and wastewater treatment including membrane bioreactor and water recycling/tertiary filtration [3]. In both research laboratories and industrial manufacturing, PVDF membranes are mainly produced by the phase inversion technique, particularly NIPS method [1, 4].

Despite those advantageous properties, PVDF membranes do encounter important issues in the applications of water/wastewater treatment. For example, PVDF membranes always have low water permeance and are susceptible to fouling due to the hydrophobic nature of the material. As shown in Table 4.2, the pure water flux of commercial membranes is normally less than 150 litre per square meter per hour under 1 bar pressure difference (LMH bar⁻¹) according to the product brochure provided by the manufacturers. This means that a large amount of membrane modules is required to supply enough membrane area and thus meeting the high demand of the processing volume. On the other hand, in the treatment of wastewater especially those containing natural organic matter, frequent cleaning steps are needed in order to remove the fouling layer and maintain the throughput of the membrane modules. Both problems will lead to increase in the costs and energy consumption in the filtration plants. Consequently, numerous research works have been focused on the optimisation of membrane structure and properties so as to enhance the membrane permeability and fouling resistance. As discussed in Chapter 4, however, complex physical-chemical factors are involved in the NIPS process [1, 4, 5], which makes it fairly difficult to control the membrane quality and almost impossible to achieve the ideal membrane structure. Moreover, although various modification approaches have been developed to improve the performance of PVDF membranes, either extra chemicals or pre-/post-treatments are involved, which will result in increase in the production cost and is unfavourable.

Inspired by the “freeze drying” method in materials engineering [6-8], a new membrane fabrication method combining oriented green solvent crystallization and polymer migration has been proposed and described in details in Chapter 4. Briefly, in the CCD method, the polymer dope solution is first cast on the casting plate and is then unidirectionally cooled to a temperature below the freezing temperature of the solvent. The unidirectional cooling is achieved by either placing the casting plate on a pre-cooled plate or immersing in a pre-cooled liquid. During the quenching process, the solvent crystallises as the temperature increases, while the polymer molecules are expelled and precipitate around the solvent crystallites. After quenching, the solvent crystallites are removed by immersing the polymer film in iced water. Basically, the CCD method uses unidirectional solvent crystallisation to produce pores and asymmetric membranes with gradually opened micro-channels can be obtained. In Chapter 4, the mechanism of the CCD method was discussed and the effects of cooling conditions, casting thickness and choice of solvents on the membrane structure and filtration performance were investigated. The preliminary results indicated that membranes with pore size down to 30 nm

could be prepared when the cooling rate was fast (Al/Al case). However, too fast cooling rates (i.e. hexane case and liquid nitrogen case) and slow cooling rates (i.e. Al/G case and G/G case) would facilitate the formation of large pores. In addition, decreasing the casting thickness would reduce the membrane pore size and the membrane flux. It was also found that the employment of different solvents could affect the sequence of phase inversion and solvent crystallisation and thus the final membrane structure. Generally, the CCD membranes prepared with dimethyl sulfoxide (DMSO) as the solvent have a typical CCD membrane structure. The DMSO CCD PVDF membranes have demonstrated excellent performance with pure water permeation flux 100 times higher than those with similar pore size prepared by the conventional NIPS processes.

In this chapter, more detailed characterisation work was conducted on the prepared CCD membranes including Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), X-ray diffraction (XRD) analysis, water contact angle measurement, pure water filtration test, fouling test, mechanical test and abrasion test. The conventional NIPS method was also employed to prepare PVDF flat sheet membranes as control samples. The characterisation results indicated that compared to traditional NIPS and thermally induced phase separation (TIPS) membranes with same pore size, the CCD membranes showed higher permeation flux after fouling and better mechanical properties, which are all crucial in real applications.

5.3 Methodology

5.3.1 Materials

Commercial PVDF (Kynar[®] K-761, $M_w = 440,000$ Da, $\rho = 1.79$ g/cm³) was purchased from Elf Atochem and was dried at 80 °C for 24 hours before use. Bovine serum albumin (BSA), DMSO, *N,N*-dimethylacetamide (DMAc), *N*-Methyl-2-pyrrolidone (NMP), ethanol, and SiC were purchased from Sigma-Aldrich, UK and were used as received.

5.3.2 Membrane Preparation

PVDF flat sheet membranes with highly asymmetric and self-assembled ordered structure were produced by CCD method, which was introduced in details in the previous chapter. The PVDF dope solutions were prepared by dissolving PVDF powder (20 wt.%) in DMSO at 80 °C or in NMP and DMAc at room temperature, and was then left in the oven at 80 °C overnight for degassing. The dope solution was then cast of a certain thickness on a casting plate, followed by unidirectionally cooling to a pre-determined temperature, which was

achieved by contacting with a pre-cooled cold plate. The materials of the cold plate and the casting plate were aluminium or glass so as to realize different thermal conductions and thus different cooling rates. After complete quenching, the frozen casting film was immersed in iced water to leach the solvent out. The water was changed regularly to remove the residual solvent. Apart from the materials of the plates, the casting thickness was varied in order to investigate its effects on the membrane morphology and properties.

Besides, the conventional NIPS method was employed to prepare PVDF membranes as the control samples using DMSO, DMAc and NMP as the solvent and deionized water as the non-solvent. The same polymer solution was cast on a glass plate at room temperature and then immediately immersed into the water bath at room temperature. The fabricated membrane was then kept in deionised water, which was changed frequently to remove the residual solvent before all the characterisations. The preparation conditions of each sample were summarised in Table 5.1.

Table 5.1 Casting conditions for the preparation of flat sheet membranes

	Sample	Solvent	Casting Thickness	Casting Plate	Cold plate/ Cooling Condition
CCD	G/G*	DMSO	1mm	6 mm Glass	6 mm Glass plate (-30 °C)
	Al/G	DMSO	1mm	6 mm Al	6 mm Al plate (-30 °C)
	Al/Al 1.0 mm	DMSO	1mm	6 mm Al	6 mm Al plate (-30 °C)
	Al/Al 0.5 mm	DMSO	0.5mm	6 mm Al	6 mm Al plate (-30 °C)
	Al/Al 0.3 mm	DMSO	0.3mm	6 mm Al	6 mm Al plate (-30 °C)
	Al/Al 0.1 mm	DMSO	0.1mm	6 mm Al	6 mm Al plate (-30 °C)
NIPS	DMSO 1.0 mm	DMSO	1.0mm	6 mm Glass	N/A
	DMSO 0.5 mm	DMSO	0.5mm	6 mm Glass	N/A
	DMSO 0.3 mm	DMSO	0.3mm	6 mm Glass	N/A
	DMAc 0.3 mm	DMAc	0.3mm	6 mm Glass	N/A
	NMP 0.3 mm	NMP	0.3mm	6 mm Glass	N/A

*: material of the casting plate/material of the cooling plate, G represents glass and Al stands for aluminum.

5.3.3 Membrane Characterisation

The wet membranes were used directly for the filtration tests, gas-liquid displacement porosimetry and the abrasion test, but were dried via the solvent (ethanol) exchange technique prior to other characterizations.

Characterisation methods including scanning electron microscopy (SEM), crystal study with XRD analysis and mechanical test are described and explained in Section 3.3.3. The membrane pore size and pore size distribution were investigated by the gas liquid displacement method, as introduced in Section 4.4.3.2.

5.3.3.1 Fourier Transform Infrared Spectroscopy

The phase structure of the PVDF membranes was analysed using an FTIR spectrometer (Perkin Elmer, Spectrum One equipped with an ATR attachment). The samples were placed on the sample holder and all spectra were recorded in the wavenumber range of 4000–600 cm^{-1} by accumulating 8 scans at a resolution of 2 cm^{-1} .

5.3.3.2 Differential Scanning Calorimetry

The melting behaviour of each membrane sample was characterized by DSC (Pyris-1, Perkin Elmer, Beaconsfield, UK) and was used to determine the percentage crystallinity of PVDF in the membranes. The samples were heated from 20 °C to 220 °C at 10 °C/min. The percentage crystallinity of PVDF in each membrane sample was calculated by the equation shown below:

$$\text{Equation 5.1} \quad \% \text{ Crystallinity} = \frac{\Delta H_m}{\Delta H_m^\circ} \times 100\%$$

where ΔH_m is the heat associated with melting (fusion) of the membrane and is obtained from the DSC thermograms, ΔH_m° is the heat of melting if the polymer was 100% crystalline and is 104.7 J/g for PVDF.

5.3.3.3 Water Contact Angle Measurement

The surface hydrophilicity of the membranes was studied by measuring the water contact angle on the surfaces of the separation layer. The measurement was conducted at room temperature using a ramé-hart Standard Goniometer (Model 250, ramé-hart instrument co., USA). In the test, 4 μL of deionised water droplets were deposited onto the membrane surface of each sample. The image was captured and the contact angle was measured based on shape analysis with the DROPImage Advanced software. At least five independent readings were taken at different sites on each membrane sample and the average value was reported.

5.3.3.4 Pure Water Permeation Test

In order to evaluate the membrane permeability, pure water permeation tests were conducted using a 300 mL dead-end filtration cell (HP4750 Stirred Cell, Sterlitech Corporation, USA). The PVDF membrane samples prepared by the CCD method were tested using the same

method as explained in Section 4.4.3.1. On the other hand, the membrane samples prepared by the conventional NIPS method were compacted at a pressure of 2 bar for 30 min prior to sample collection at 1 bar. The permeance of the membrane was calculated based on the equation shown below:

Equation 5.2
$$J = \frac{V}{A \times t}$$

where J is the water flux, V is the permeate volume, A is the effective membrane area, t is the time of permeate collection.

5.3.3.5 BSA Fouling Test

The fouling test was conducted using a cross-flow filtration cell (CF042 Crossflow Assembly, Sterlitech Corporation, USA), and BSA was employed as a model protein to investigate the fouling resistance of the CCD Al/Al 1.0mm PVDF membrane as an example. In the test, 1.0 g/L BSA aqueous solution was circulated through the feed side of the filtration cell, and the weight of the permeate was recorded for 24 h by a computer in real time. For the permeability recovery test, in each cycle pure water was first used as the feed solution for 30 min, followed by BSA solution for another 30 min. The membrane sample after BSA fouling was cleaned in an ultrasound bath for 5 min, and the cleaning step was repeated 3 times before the next cycle. In each test, the trans-membrane pressure was fixed at 1 bar and the permeate weight was recorded by a computer.

For the static adsorption fouling test, each membrane sample was cut to fixed area of 43 cm² and was then put into 15 mL 1.0 g/L BSA solution. After 24 h at room temperature, the membrane was rinsed and dried at 80 °C to obtain the weight of each sample. Concentration difference of the BSA solution before and after the adsorption test was measured using a UV spectrophotometer (UV-1800, Shimadzu, UK) at a fixed wavelength of 278 nm. Then the weight of BSA adsorbed per membrane weight was calculated and recorded for each sample.

5.3.3.6 Abrasion Test

In this work, the abrasion test was carried out using a 400 mL dead-end filtration cell (Stirred Cell Model 8400, Merck Millipore, Germany). A 2000 mg/L SiC suspension was prepared and used to simulate the accelerated abrasion condition in wastewater treatment. The wet membrane sample was placed in the filtration cell, and 300 mL of the SiC suspension was filled and then stirred at 400 RPM for 2 weeks. Subsequently, the membrane sample was washed under ultrasound for 10 min to remove all the debris worn away from the membrane during the test. Then the change in the membrane structure was observed using SEM.

5.4 Results and Discussions

In Chapter 4, it was found that the pure water permeation flux of the CCD membranes were substantially higher than the commercial membranes. Since most commercial membranes are manufactured from modified PVDF to increase surface hydrophilicity, pure PVDF membranes using the same polymer solutions but via the conventional NIPS method were prepared as the control samples. In this section, the difference between CCD membranes and NIPS membranes will be discussed in details in terms of filtration performance including pure water flux and BSA fouling test, surface hydrophilicity, membrane structure from macro level to crystal level, and mechanical properties including mechanical strength and abrasion resistance.

5.4.1 Filtration Performance

Table 5.2 Permeation characteristics and water contact angle of CCD PVDF membranes, NIPS PVDF membranes and some commercial PVDF membranes

Membrane Type		Pure water flux (LMH bar ⁻¹)	Pore size (nm)	Water contact angle (°)
CCD membranes*	G/G 1.0 mm	10998 ± 407	345 ± 26	99.5 ± 4.8
	Al/G 1.0 mm	5017 ± 547	119 ± 10	93.4 ± 1.6
	Al/Al 1.0 mm	861 ± 78	45 ± 3	89.5 ± 3.5
	Al/Al 0.5 mm	570 ± 37	29 ± 3	84.5 ± 4.2
	Al/Al 0.3 mm	608 ± 82	30 ± 9	76.7 ± 7.1
	Al/Al 0.1 mm	486 ± 28	38 ± 11	62.7 ± 14.8
NIPS membranes*	DMSO 1.0 mm	6.9 ± 3.4	35 ± 7	87.7 ± 8.6
	DMSO 0.5 mm	6.1 ± 1.2	45 ± 9	74.9 ± 5.6
	DMSO 0.3 mm	9.3 ± 5.8	54 ± 12	70.7 ± 2.8
	NMP 0.3 mm	2.3 ± 2.6	61 ± 11	66.4 ± 11.7
	DMAc 0.3 mm	2.7 ± 0.5	< 18	65.1 ± 3.8
Commercial membranes**	DOW	40 - 120	30	Modified hydrophilic PVDF
	EVOQUA	20	40	
	KOCH PURON®	100	30	
	GE ZeeWeed 1500	135	20	
	TORAY	30 (MBR)	80	
	Pall	> 3000	200	

	Pall	> 8200	450	
	TriSep TM10	90	200	
	Hydranautics HYDRAcap®	34 - 110	80	

*: Sample names are ended with casting thickness.

**: Pore sizes are nominal pore sizes provided by the manufacturers; water flux was converted from product brochures of the membrane modules, but operation pressure and other conditions are unclear.

As summarised in Table 5.2, the pure water permeation flux of the CCD membranes is substantially higher than the commercial membranes. Especially for the MF membranes with pore sizes of 119 nm and 345 nm, the pure water flux reached stunning 5017 and 10998 LMH bar⁻¹, respectively. Considering a fact that most commercial membranes are prepared from modified PVDF to increase surface hydrophilicity, to make fair comparisons, we also prepared pure PVDF membranes using the same polymer dope solutions but via the conventional NIPS method. The NIPS pure PVDF membranes showed pure water flux of less than 10 LMH bar⁻¹ (Table 5.2), which are two orders of magnitude lower than the CCD Al/Al membrane with similar pore size.

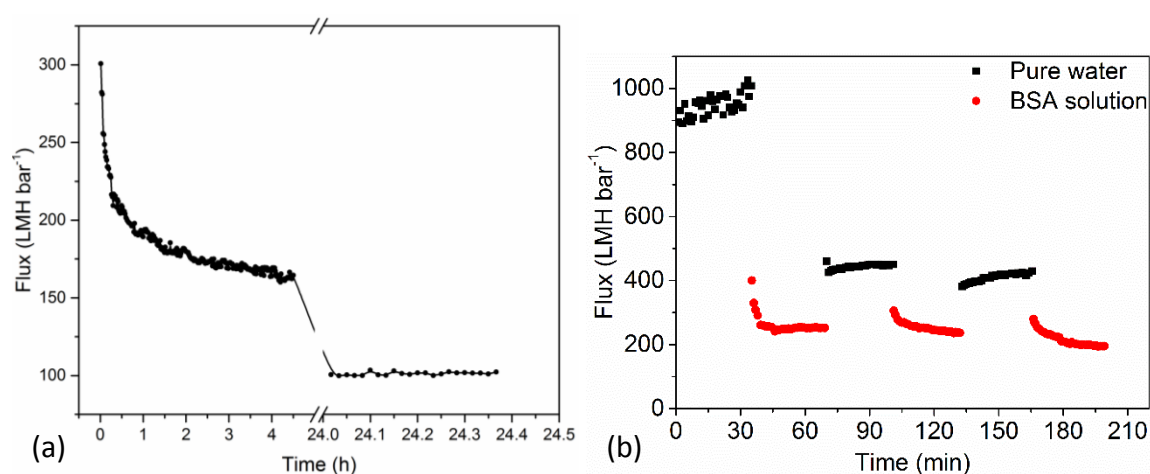


Figure 5.1 BSA fouling test result of a CCD Al/Al 1.0 mm PVDF membrane: (a) permeation flux vs. time over 24 hours, (b) permeation flux during three cycles of pure water/BSA solution permeation tests

Fouling tests with a 1.0 g/L BSA solution revealed that the CCD Al/Al 1.0 mm pure PVDF membranes had lower tendency of fouling, which showed a slow and gradual decline of the permeation flux from 300 LMH to a steady flux of 100 LMH after being tested for 24 h (Figure 5.1 (a)). Considering that the tendency of fouling is closely related to the permeation flux [9], i.e. higher permeation flux normally leads to more severe fouling, the fouling rate of

the CCD membrane is impressive compared with other NIPS and TIPS pure PVDF membranes [10-13]. As being recommended by most commercial membrane suppliers, MF/UF membrane modules should be periodically cleaned with an interval of 30-40 minutes after operation in order to resume permeability. The flux recovery of the membrane after cleaning was also tested and is shown in Figure 5.1 (b). The pure water flux of the CCD membrane could not be fully recovered after fouling, which is in agreement with other NIPS or TIPS PVDF membranes [10-13]. However, even after fouling, the CCD UF membranes still gave permeation flux of c.a. 200 LMH bar⁻¹, which is about one order of magnitude higher than conventional PVDF membranes (Table 5.3). The CCD fabrication process can bring optimized membrane structures, but cannot alter the nature of the membrane material. It has been well known that pure PVDF material has high affinity to proteins, therefore BSA is difficult to be removed from the membrane surface. On the other hand, the surface nature of the membrane can be changed by modification to reduce fouling, as it has been intensively studied in the membrane society and it would further improve the anti-fouling property [1, 2, 10, 13, 14].

Table 5.3 Comparison of cross-flow BSA fouling test results for pure PVDF membranes made by NIPS, TIPS and CCD methods

Ref	Preparation Method	Experiment	Results
[11]	TIPS	Pure PVDF, 50 nm pore size, 250 LMH/bar, BSA 1g/L	BSA flux decreased from ~80 LMH to ~27 LMH (33.7%) in 2h.
[12]	NIPS	Bare PVDF, 20 nm pore size, BSA 1g/L	BSA flux decreased to 10% at 0.05 m ³ permeated water per m ² membrane area.
[10]	NIPS	Pure PVDF, unknown pore size, BSA 1g/L	BSA flux decreased to 33.5% in 1h.
[13]	NIPS	Pure PVDF, unknown pore size, MWCO>>162 kDa, BSA 1g/L	BSA flux decreased to <10% in 2.5 h.
This work	CCD Al/Al	Pure PVDF, 45 nm pore size, BSA 1g/L	BSA flux decreased to 64% in 1 h, 59% in 2 h, and 33% after 24 h.

Static adsorption fouling test was also conducted with all the 0.3mm thick membranes and the results are summarised in Table 5.4. It was found that both NMP and DMAc NIPS membranes showed low BSA adsorption, whereas the DMSO NIPS membrane had significantly higher protein adsorption, although these three NIPS membranes have a very

similar phase composition with the majority of α phase PVDF. For the CCD membrane, its BSA adsorption was even more severe than the DMSO NIPS membrane. It seems that the solvent is more important than the crystal phase in the static protein adsorption test. The accessible surface area is one factor that might affect the adsorption results significantly. For the CCD membranes, the accessible surface area is very high since the pores are highly interconnected. However, for the NIPS membranes, the accessible surface area is affected by the number of dead pores, which is in turn affected by the solvent used in the polymer solution.

Table 5.4 Static adsorption fouling test results of the CCD and NIPS membranes

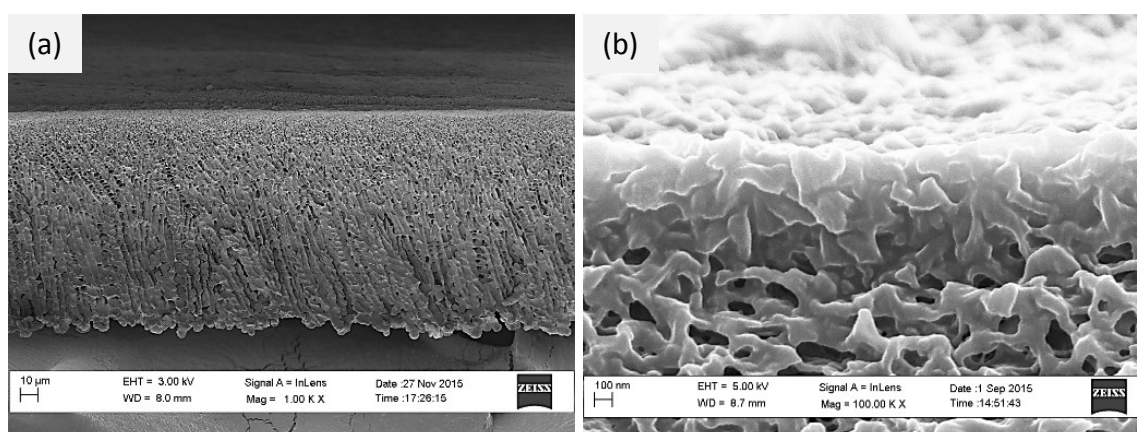
Sample	NMP/NIPS	DMAc/NIPS	DMSO/NIPS	DMSO/CCD(Al/Al)
BSA Adsorption (mg/g)	1.49 ± 0.32	0.17 ± 0.10	12.01 ± 0.57	16.01 ± 0.20

5.4.2 Membrane Hydrophilicity

In the literature, change in the surface hydrophilicity is often considered as an important factor that influences the water permeation of membranes [1, 2]. In this work, however, water contact angle measurement showed that the CCD membranes had similar or even slightly higher contact angles compared with those NIPS membranes (Table 5.2). The large contact angle agrees with the hydrophobic nature of pure PVDF material. Thus, the high water flux can be directly related to the unique structure of the membrane prepared by the proposed method.

5.4.3 Membrane Structure

5.4.3.1 Morphological Structure



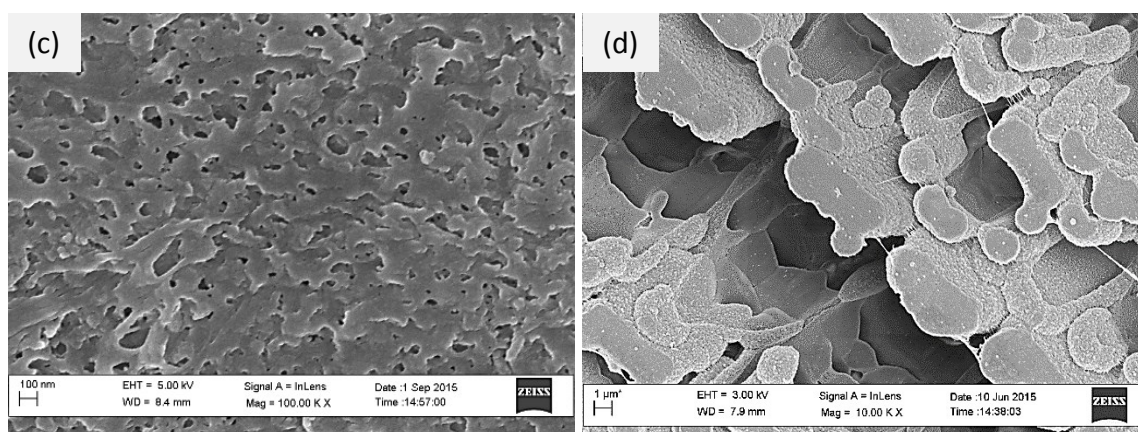
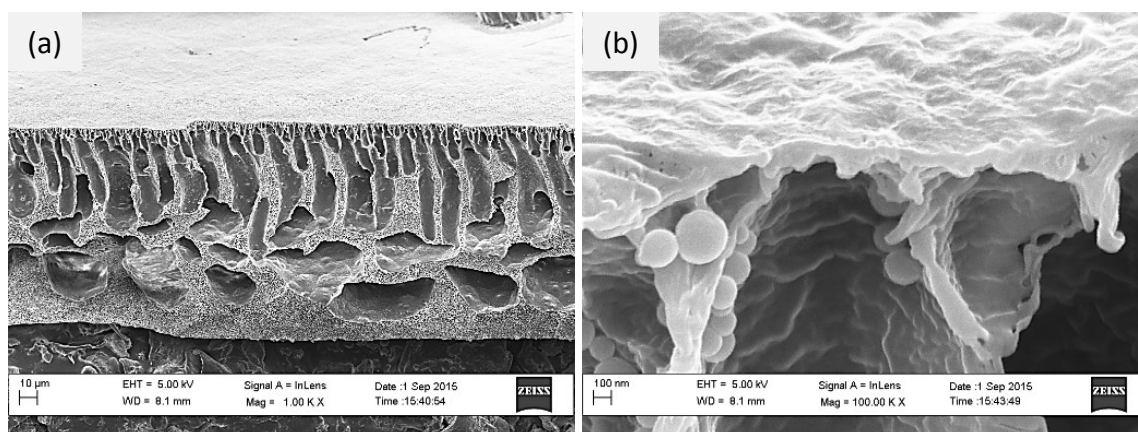


Figure 5.2 SEM images of a CCD Al/Al 0.3mm PVDF membrane: (a) overview of cross section; (b) close cross-sectional view of the separation layer; (c) surface of the separation layer; (d) back surface of the supporting layer

Fixing the casting thickness at 0.3mm, the difference in membrane morphologies between the CCD and NIPS membranes is studied. As discussed in Section 4.5.1, in the CCD membranes, a thin separation layer is supported by numerous very well arranged micro-channels whose size gradually increases from the separation layer (Figure 5.2 (a)). The cross section image of the membrane shows clearly a number of tortuous pores in the separation layer (Figure 5.2 (b)), corresponding to the intensively scattered pores on the membrane surface (Figure 5.2 (c)). Furthermore, the supporting layer of the CCD membranes is composed of fully opened, oriented and interconnected micro-channels, which actually give negligible resistance to water permeation (Figure 5.2 (d)).



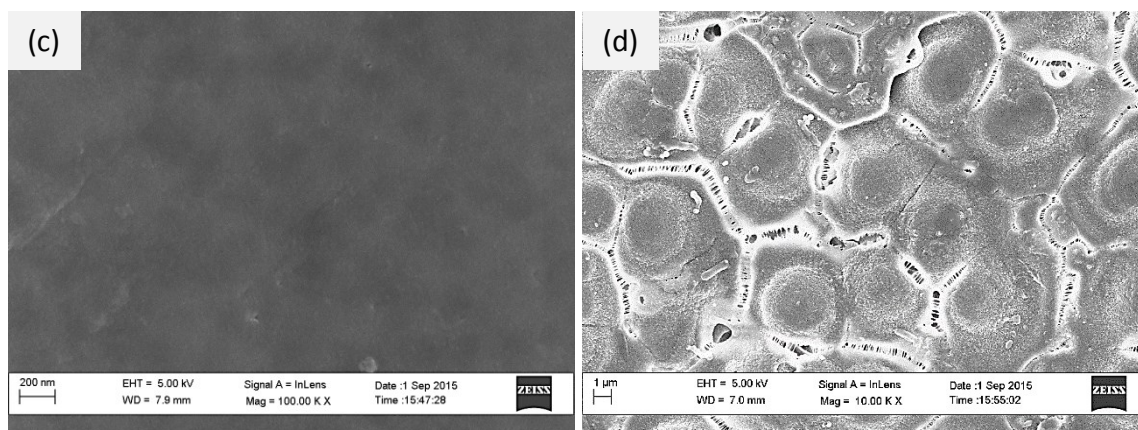
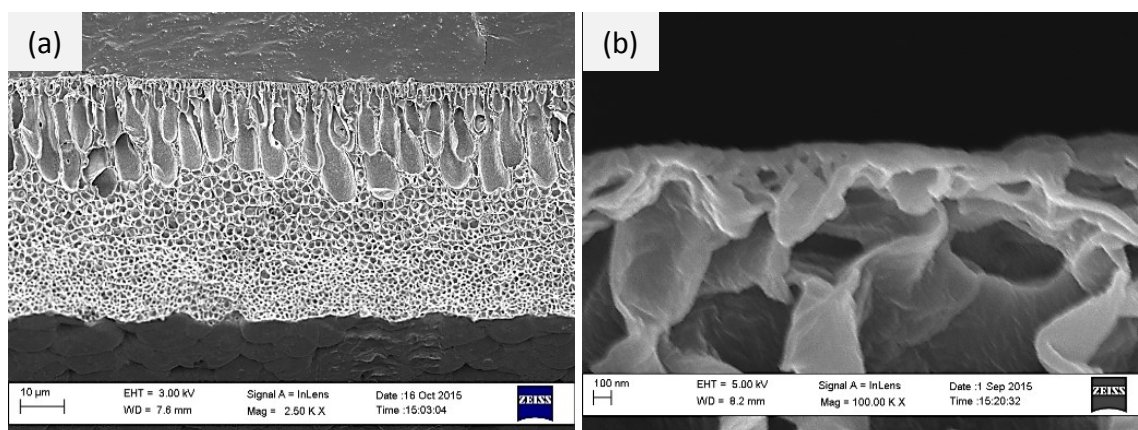


Figure 5.3 SEM images of a NIPS DMSO 0.3mm PVDF membrane: (a) overview of cross section; (b) close cross-sectional view of the separation layer; (c) surface of the separation layer; (d) back surface of the supporting layer

By comparison, the NIPS membranes all have typical asymmetric structures with a skinned top layer supported by a region of finger-like voids and then a sponge-like layer (Figure 5.3 (a), Figure 5.4 (a) and Figure 5.5 (a)). In particular, the formation of macrovoids was clearly observed in the cross section of the NIPS DMSO 0.3mm PVDF membrane (Figure 5.3 (a)). Although the skinned top layers of the NIPS membranes are thinner compared to the CCD membranes (Figure 5.3 (b), Figure 5.4 (b) and Figure 5.5 (b)), only few pores on membrane surface can be observed within the scanned area of SEM, implying the very low surface porosity (Figure 5.3 (c), Figure 5.4 (c) and Figure 5.5 (c)). In contrast, the CCD membrane has a very porous separation layer.



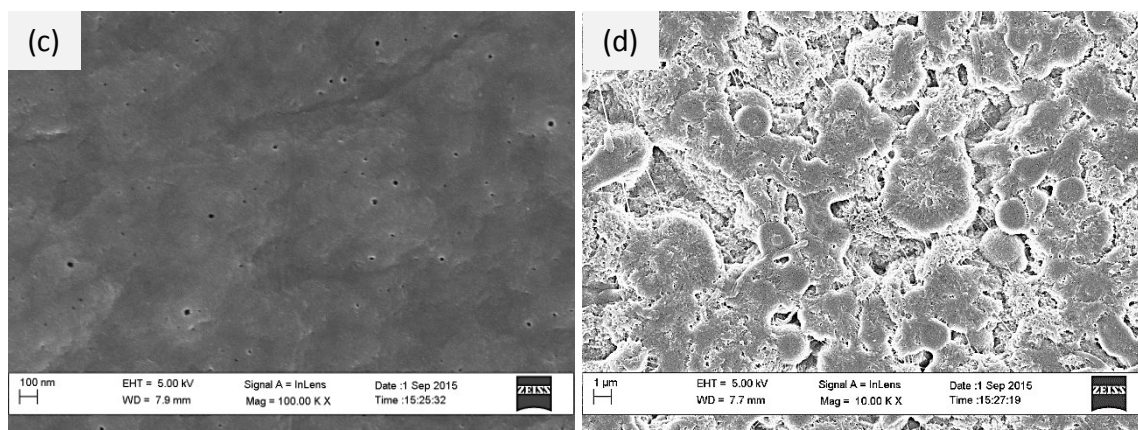
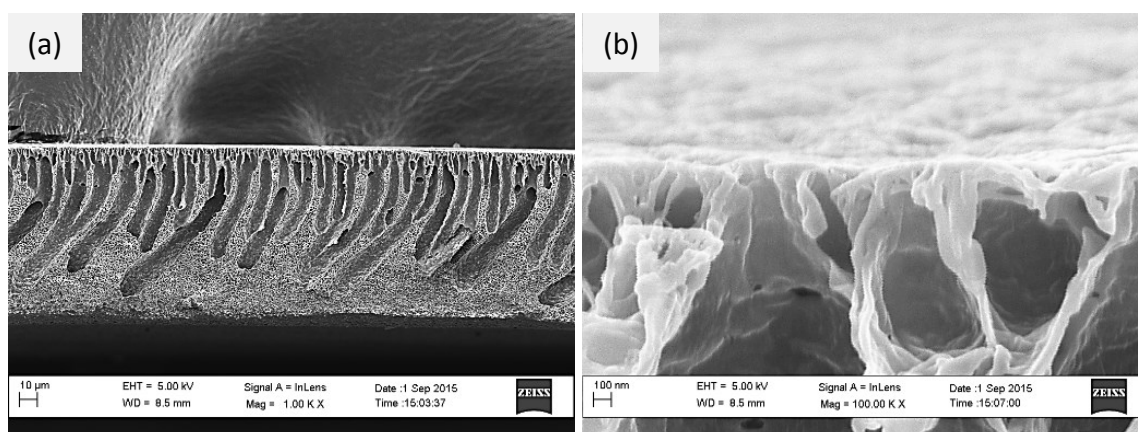


Figure 5.4 SEM images of a NIPS DMAc 0.3mm PVDF membrane: (a) overview of cross section; (b) close cross-sectional view of the separation layer; (c) surface of the separation layer; (d) back surface of the supporting layer

Besides, the NIPS membrane has a largely closed backside and back surface (Figure 5.3 (d), Figure 5.4 (d) and Figure 5.5 (d)), which would not only contribute to the total transport resistance, but also tend to intensify the fouling problem as foulant would accumulate in the supporting layer. Such foulant accumulation in the supporting layer, however, can be avoided in the CCD membranes by the fully opened micro-channels. The effect of the membrane morphology on its fouling resistance has been verified in the BSA fouling test, as discussed in Section 5.4.1.



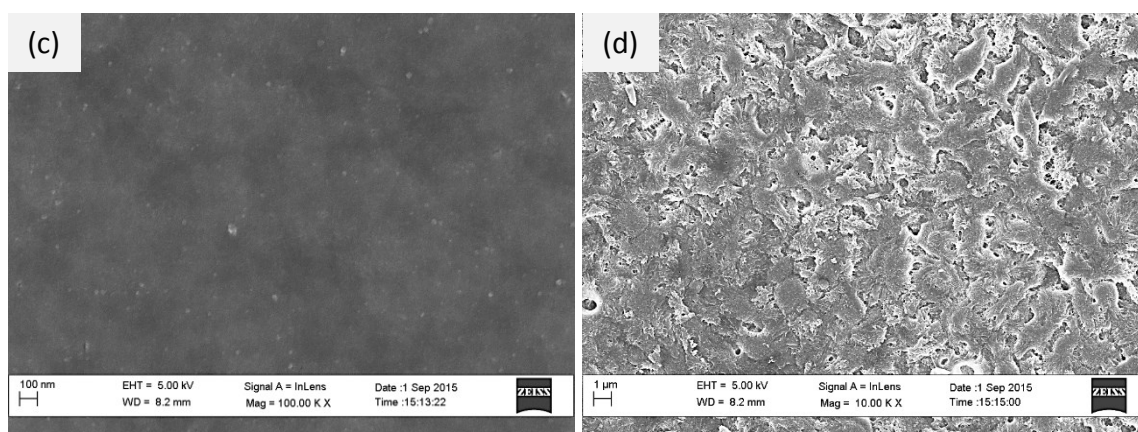
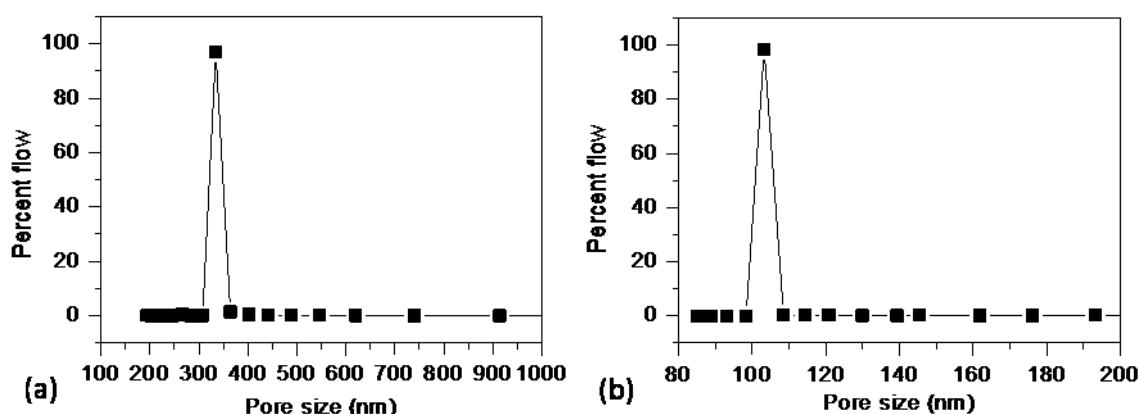


Figure 5.5 SEM images of a NIPS NMP 0.3mm PVDF membrane: (a) overview of cross section; (b) close cross-sectional view of the separation layer; (c) surface of the separation layer; (d) back surface of the supporting layer

5.4.3.2 Pore Structure

Figure 5.6 shows the typical pore size distribution of the CCD and NIPS PVDF membranes. All the measurements used the same pressure steps to ensure fair comparisons. Figure 5.6 (a) shows a CCD G/G 1.0 mm sample, which has a sharp peak at 334 nm with a percent flow of 97.0%; Figure 5.6 (b) shows a CCD Al/G 1.0 mm sample, which has a sharp peak at 103 nm with a percent flow of 98.3%; and Figure 5.6 (c) shows a CCD Al/Al 1.0 mm sample that has a peak at 40 nm with a percent flow of 72.0%. On the other hand, the membranes prepared by the NIPS method displayed much broader pore size distributions. The NIPS DMSO 1mm sample shows a maximum percent flow of 18.9% at 38 nm (Figure 5.6 (d)); the NIPS DMSO 0.3 mm sample shows a maximum percent flow of 15.5% at 56 nm (Figure 5.6 (e)); and the NIPS NMP 0.3 mm sample shows a maximum percent flow of only 8.4% at 57 nm (Figure 5.6 (f)). The NIPS DMAc samples could not be measured, either due to the extremely low porosity, or because the pores are smaller than the testing limit of the equipment (18.6 nm).



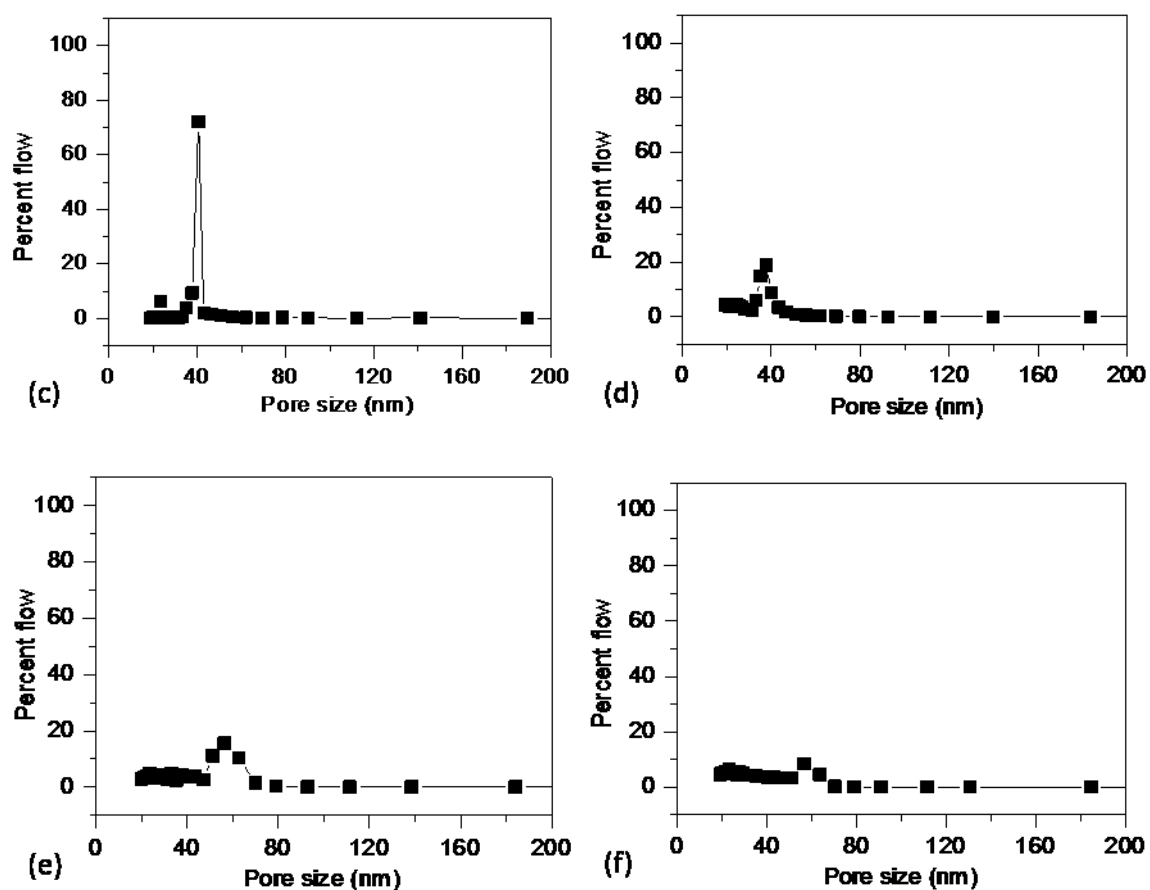


Figure 5.6 Pore size distribution of PVDF membranes measured by the gas-liquid displacement method: (a) CCD G/G 1.0 mm sample; (b) CCD Al/G 1.0 mm sample; (c) CCD Al/Al 1.0 mm sample; (d) NIPS DMSO 1.0 mm sample; (e) NIPS DMSO 0.3 mm sample; (f) NIPS NMP 0.3 mm sample

5.4.3.3 Crystal Structure

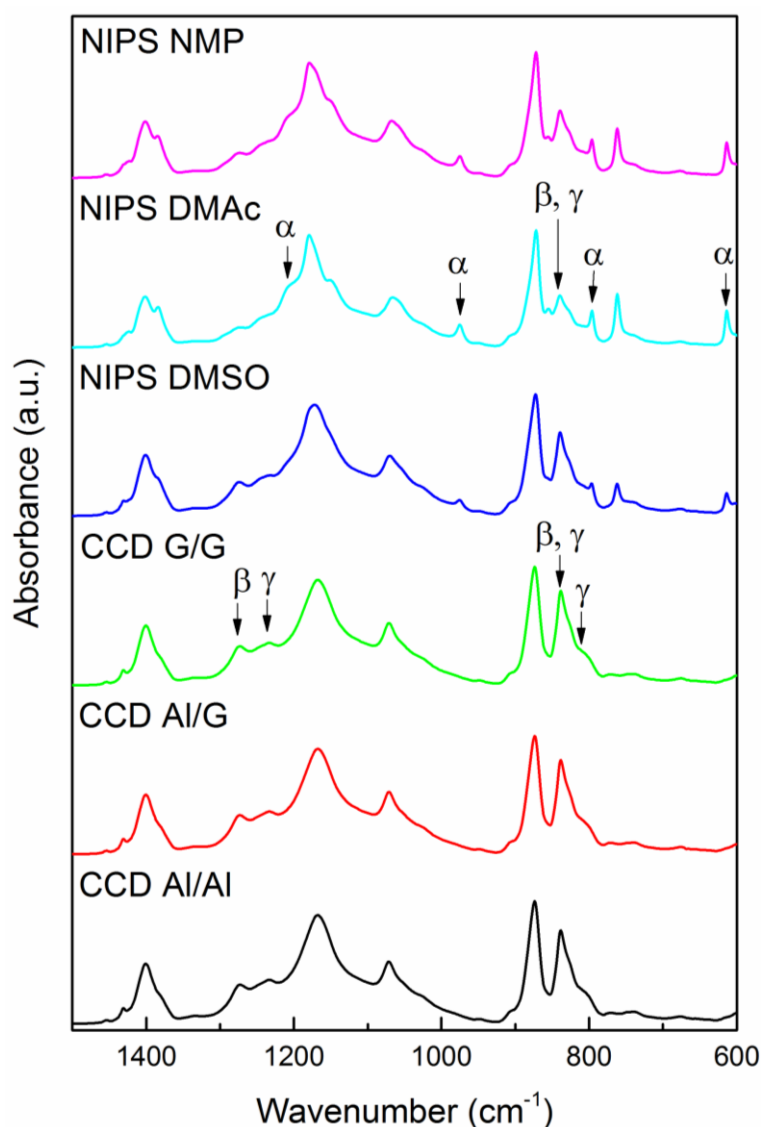


Figure 5.7 FTIR spectra of the CCD and NIPS membranes

The PVDF crystal structure in the CCD and NIPS membranes were investigated using FTIR, XRD and DSC. As shown in Figure 5.7, the bands at 615, 764, 796, 976 and 1215 cm^{-1} are assigned to the characteristic peaks of α phase and can be clearly observed in the NIPS membranes. On the other hand, the bands at 840 and 1275 cm^{-1} are the characteristic of β phase absorption, and γ phase can be well identified from the peaks at 811, 840 and 1233 cm^{-1} . It can be seen that NIPS membranes all show intensive peaks of α phase, together with peaks from β phase and γ phase, whereas for the CCD membranes, all peaks of α phase disappeared.

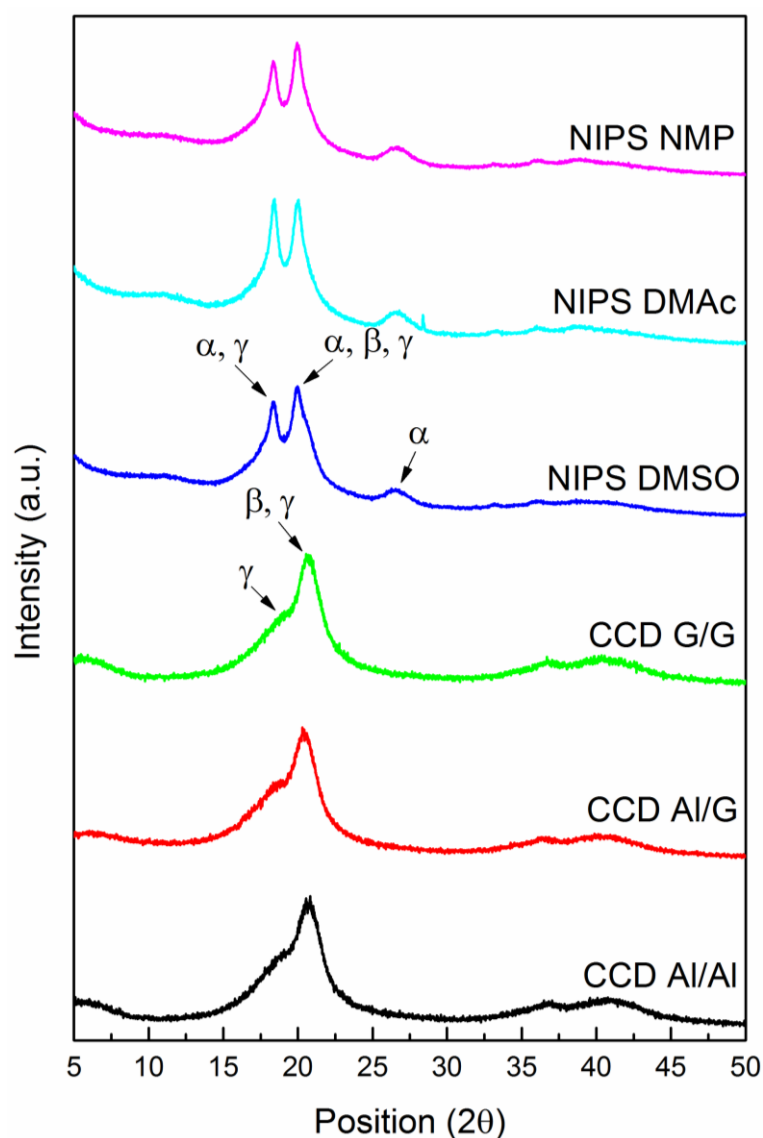


Figure 5.8 XRD patterns of the CCD and NIPS membranes

Similar conclusions could be drawn from the XRD analysis, as shown in Figure 5.8. The CCD membranes are composed of mainly β phase (the sharp diffraction peak at 20.6°) and also γ phase PVDF crystallites (peaks at 18.6° and 20.6°), while the existence of α phase PVDF could be observed in the NIPS membranes (peaks at 18.3° , 19.9° and 26.5°). The crystallinity of the CCD membranes was also evaluated by DSC and was around 60%, as shown in Figure 5.9.

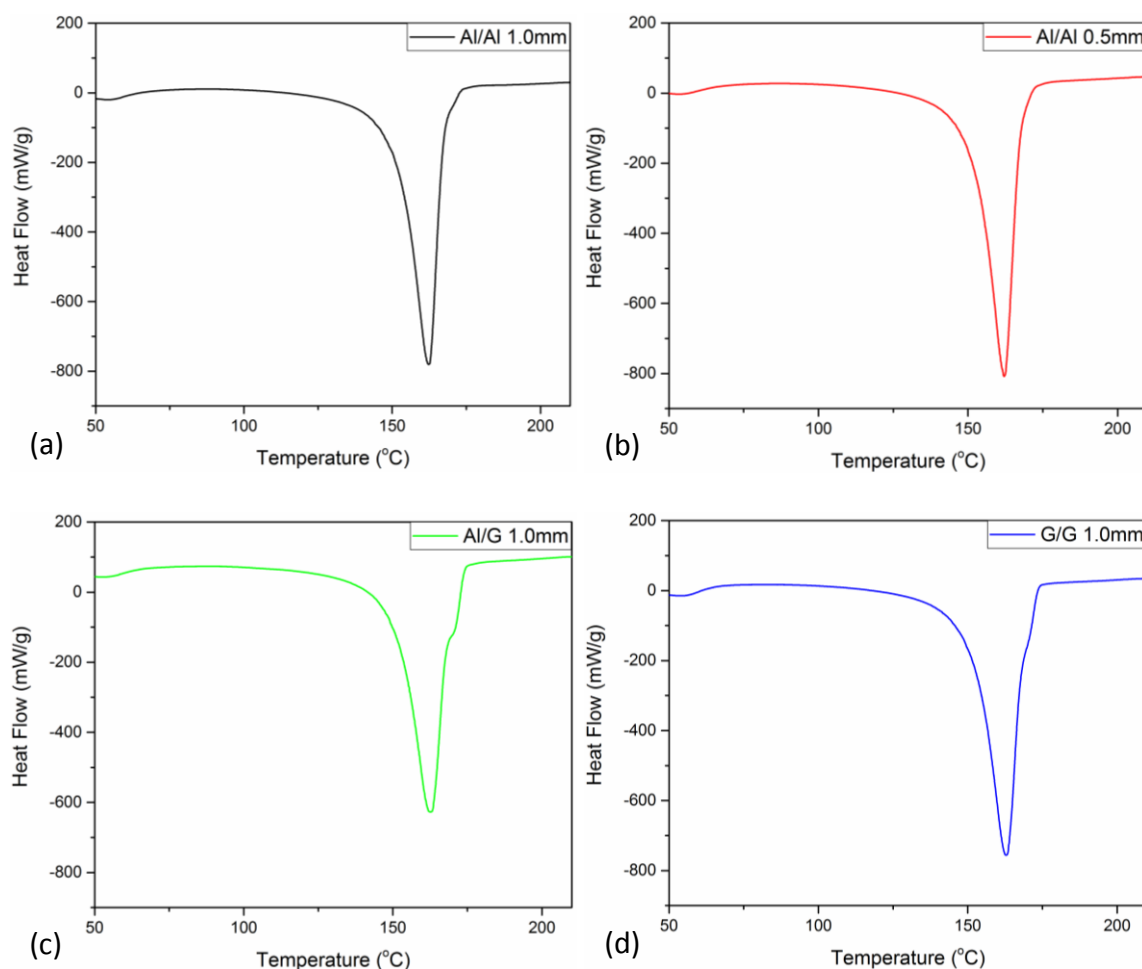


Figure 5.9 DSC results of the CCD membranes: (a) Al/Al 1.0 mm, crystallinity 59%; (b) Al/Al 0.5 mm, crystallinity 62%; (c) Al/G 1.0 mm, crystallinity 62%; (d) G/G 1.0 mm, crystallinity 64%

5.4.4 Mechanical Properties

5.4.4.1 Mechanical Strength

The mechanical strength of the CCD membranes was investigated and the results of the tensile test are listed in Table 5.5. It is interesting to find that with a faster cooling rate used during the membrane fabrication process, the membrane shows better mechanical properties in terms of higher fracture load, longer elongation and higher tensile stress. It is reasonable to attribute this trend to the microstructural change in the membrane due to the different cooling rates. With a faster cooling rate, the CCD membrane has smaller micro-channels, and the number of the micro-channel would be larger. This assumption agrees with the proposed membrane formation mechanism and is confirmed by SEM images. With smaller but more micro-channels, the stress would be better distributed in the membrane and the energy would be easier to be dissipated by deformation, and fatal damages would be less likely to happen.

Table 5.5 Tensile test results of CCD membranes

Sample name	Al/Al 1.0 mm	Al/G 1.0 mm	G/G 1.0 mm
Maximum Load (N)	12.0 ± 3.0	9.0 ± 2.8	8.0 ± 0.8
Elongation at Maximum Load (%)	47.8 ± 5.9	26.3 ± 4.9	16.4 ± 6.8
Tensile Stress (MPa)	2.4 ± 0.6	1.9 ± 0.6	1.9 ± 0.2
Young's Modulus (MPa)	68.1 ± 12.8	75.2 ± 13.1	66.5 ± 9.2
Maximum water speed* (m/s)	23.6	20.1	18.8

*: Maximum water speed was calculated based on a flat-sheet membrane of dimensions 1×2 m² (width $\times$ length), water flows along the length direction.

Furthermore, since the CCD membranes show increased flux as the thickness increases, excellent mechanical properties and high flux can be obtained simultaneously. For example, the CCD Al/Al membranes with 1 mm casting thickness and 1 cm width showed a 12 N fracture tensile force in the tensile test (Table 5.5). This means that such a flat-sheet membrane of dimensions 1×2 m² (width $\times$ length) can handle the drag force produced by flowing water along the length direction with a speed of 23.6 m s^{-1} . The value is much higher than the practical flow speeds used in real applications, which is normally less than 6 m s^{-1} .

On the other hand, the CCD membranes showed low elongation ratios at the breaking point ($< 50\%$), while it is often higher than 100% for the commercial NIPS PVDF membranes. This means that the CCD membranes are more rigid compared with the conventional NIPS membranes. The high rigidity of the CCD membranes is probably caused by the tightly connected PVDF grains presented in the supporting layer that makes sliding along grain boundaries difficult, together with the high crystallinity of PVDF and the absence of α -phase [15-17]. As shown in Figure 5.2 (d), the tightly connected PVDF grains and grain boundaries are clearly observed, especially in the supporting layer of the membranes. The formation of tightly connected PVDF grains and grain boundary might be attributed to solvent crystallisation. After DMSO forms solid crystals, the PVDF is jammed into the space between DMSO crystals, and therefore the PVDF is compressed, forming rather dense PVDF grains. This is distinct from the NIPS membranes, in which a large portion of α -phase PVDF presents (Figure 5.7 and Figure 5.8), and PVDF grains are normally loosely connected (Figure 5.3, Figure 5.4 and Figure 5.5).

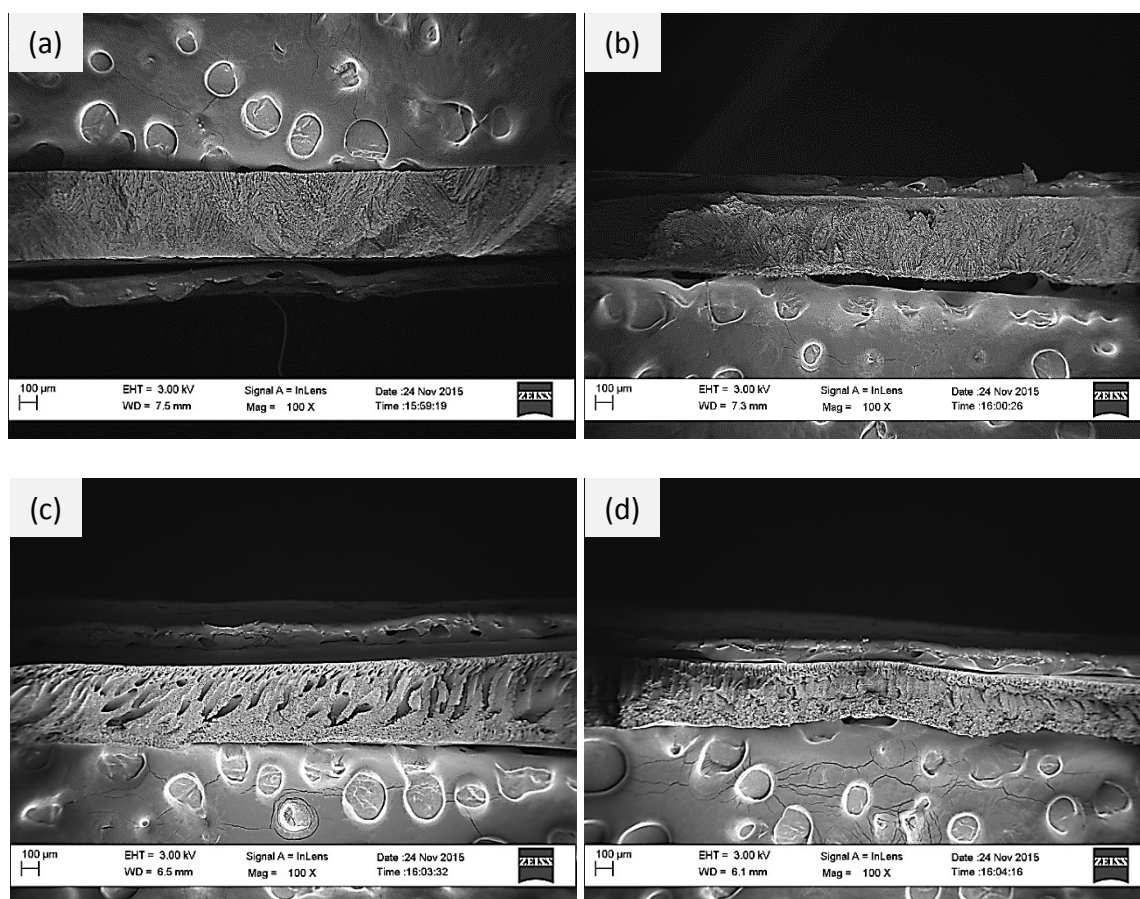


Figure 5.10 CCD Al/Al 1.0 mm PVDF membrane and NIPS DMSO 1.0 mm PVDF before and after high-pressure gas-liquid displacement measurements that reached 35 bar: (a) untested CCD membrane with thickness of $460 \pm 5 \mu\text{m}$; (b) tested CCD membrane with thickness of $435 \pm 15 \mu\text{m}$; (c) untested NIPS membrane with thickness of $440 \pm 20 \mu\text{m}$; (d) tested NIPS membrane with thickness of $330 \pm 30 \mu\text{m}$

Together with the unique structure of very well oriented micro-channels and gradually changed pores, the high rigidity helps the CCD membrane to resist high pressure. As an example, the CCD Al/Al membrane with 1 mm casting thickness was able to maintain their original thickness after the porosimetry test under a high pressure at 35 bar (Figure 5.10). On the contrary, the NIPS membranes were severely compressed with the lower part of the finger-like voids collapsed after the same test, and the thickness was reduced to 3/4 of the original value (Figure 5.10). Moreover, the CCD membranes can even withstand high-pressure mercury intrusion porosimetry tests (Section 4.5.2), whereby NIPS membranes cannot handle.

5.4.4.2 Abrasion Resistance

Membrane wearing is an important issue that current polymeric membranes always encounter during the long-term operation, and is normally inevitable in applications of water and wastewater treatments. In the filtration processes, the abrasive materials, mainly suspended

particles in the feed solution, compresses and grinds the membrane surface under the operating pressure with a high flow rate [18]. The wearing problem compromises the stability and durability of PVDF membranes, especially when the solid content is high. Thus, developing abrasion-resistant membranes will be meaningful for extending the lifetime of membrane modules. In this work, apart from the standard mechanical test, abrasion tests using an abrasive SiC suspension in a stirring cell were conducted in order to study the abrasion resistance of the membranes. With the experimental method employed for the abrasion tests, it is known that the most severe damages occur at the centre part of the membrane [19], therefore all SEM images given here were taken from the centre of the membranes for fair comparisons.

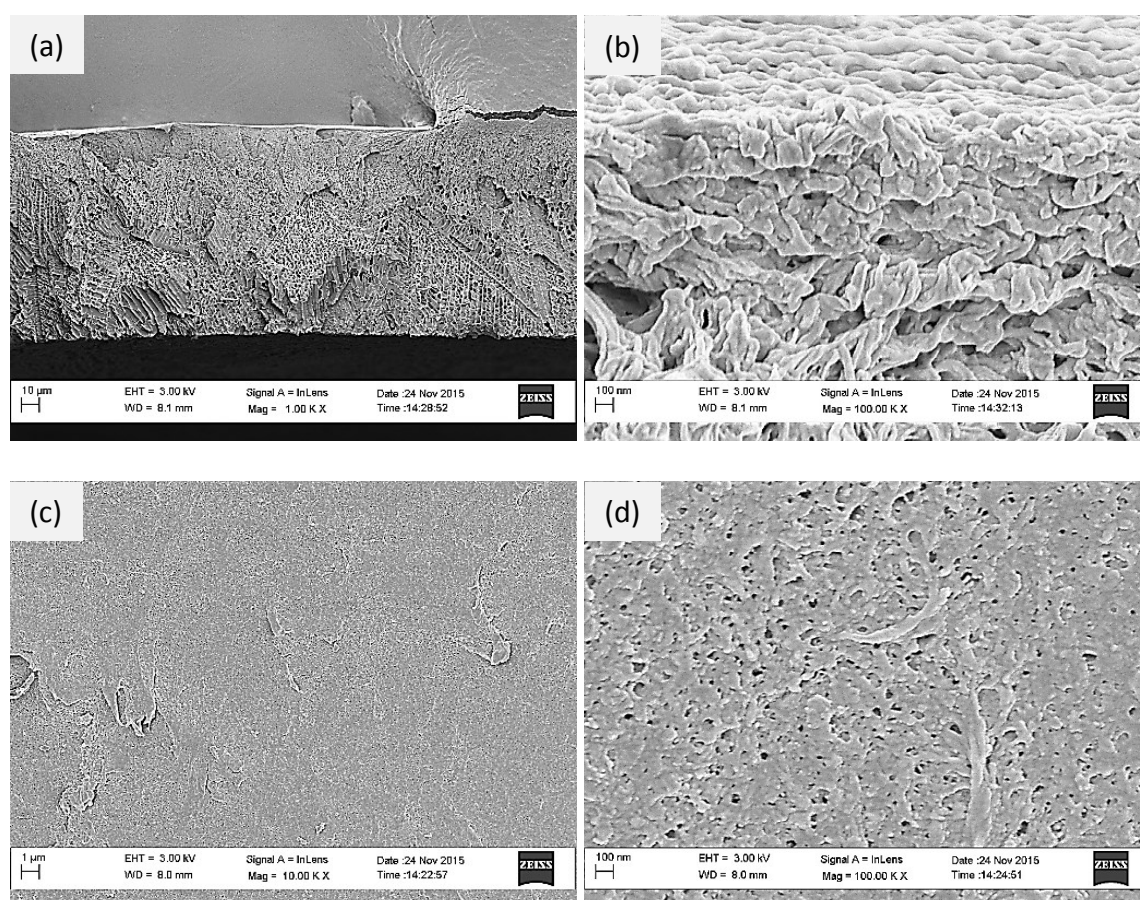


Figure 5.11 SEM images of a CCD Al/Al 0.3 mm PVDF membrane after the abrasion test for 2 weeks: (a) the cross-sectional overview; (b) a cross-sectional view close to the separation layer; (c) overview of the membrane surface; (d) high magnification image of the top separation layer

For the CCD Al/Al 0.3 mm membrane, it essentially kept the original pore structure in the separation layer and the whole membrane structure after the abrasion test. Although some extent of wearing can be found on the membrane surface, where debris was observed (Figure 5.11 (c)), the pore size on the surface and in the separation layer was not affected (Figure 5.11(b))

and (d)). And in the Figure 5.11 (b), it can be seen that the thickness of the separation layer basically did not change compared with the untested same type of membrane shown in Figure 5.2. This means that the wearing of the membrane under such accelerated test was very slight.

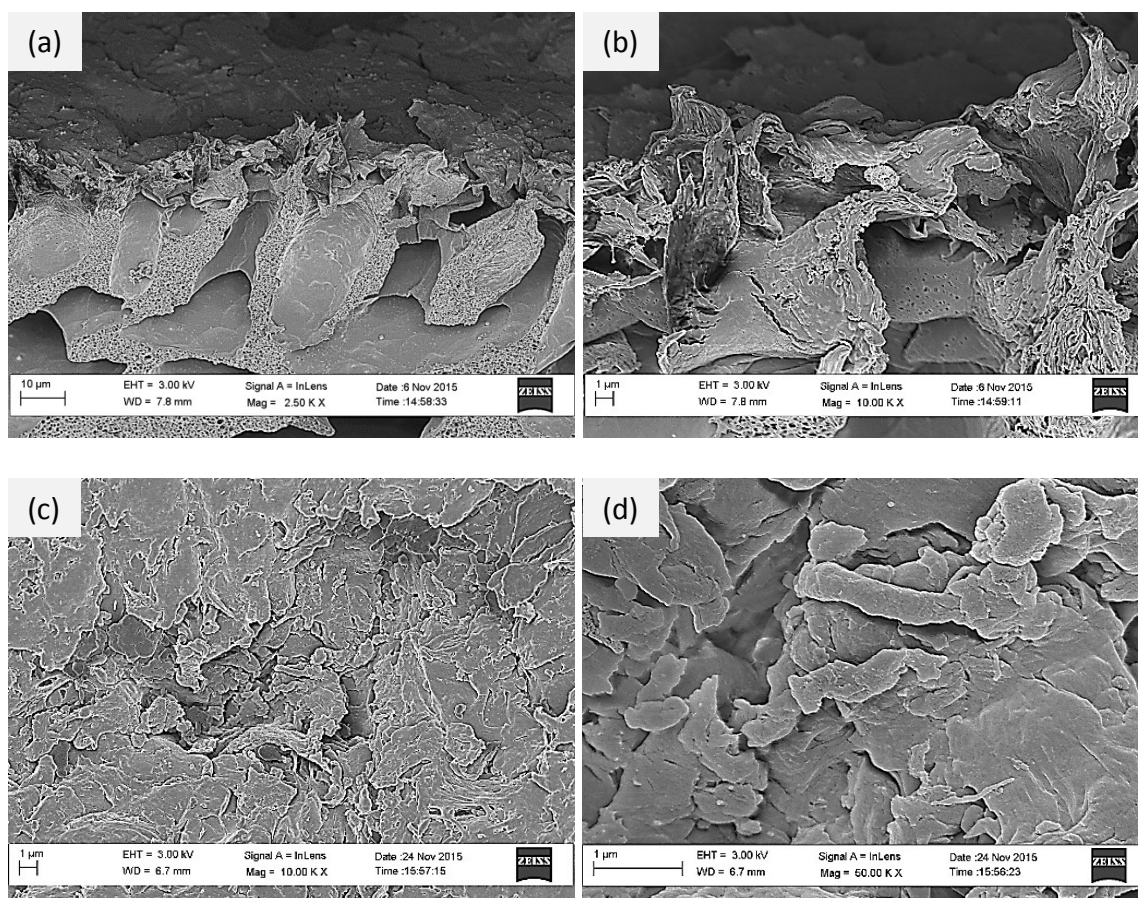


Figure 5.12 SEM images of a NIPS DMSO 0.3 mm PVDF membrane after the abrasion test for 2 weeks: (a) the cross-sectional overview; (b) a cross-sectional view close to the separation layer; (c) overview of the membrane surface; (d) high magnification image of the top separation layer

For the NIPS DMSO 0.3 mm membrane, the top separation layer was completely destroyed after the abrasion test. As shown in Figure 5.12, it can be seen that there was only debris remained at the top layer and the separation layer was gone.

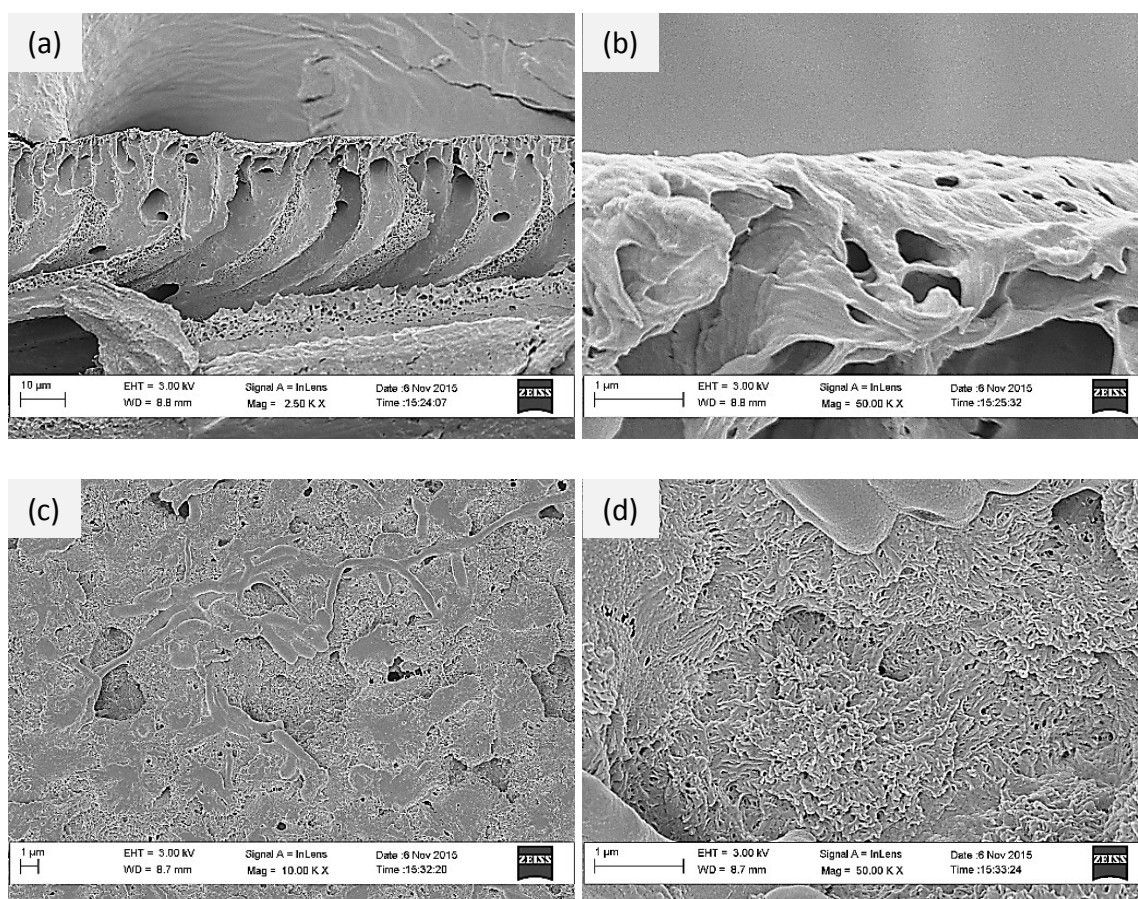
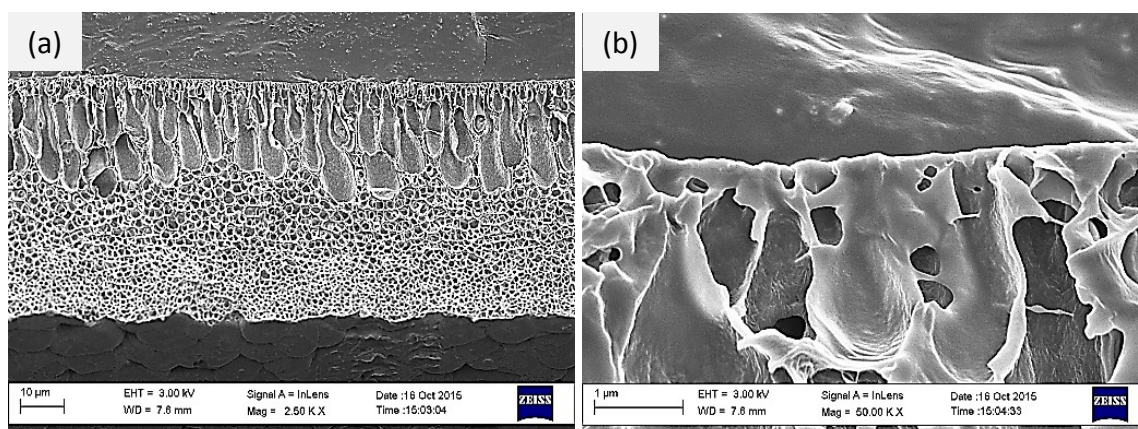


Figure 5.13 SEM images of a NIPS NMP 0.3 mm PVDF membrane after the abrasion test for 2 weeks: (a) the cross-sectional overview; (b) a cross-sectional view close to the separation layer; (c) overview of the membrane surface; (d) high magnification image of the top separation layer

For the NIPS NMP 0.3 mm membrane, the extent of wearing is less than the DMSO sample and the top layer still remains (Figure 5.13 (a)). However, the top layer has been largely deformed and the pore structure has been completely altered (Figure 5.13 (b)). Big holes appear on the membrane surface and the surface microstructure has become very rough with apparently worn parts (Figure 5.13 (c) and (d)).



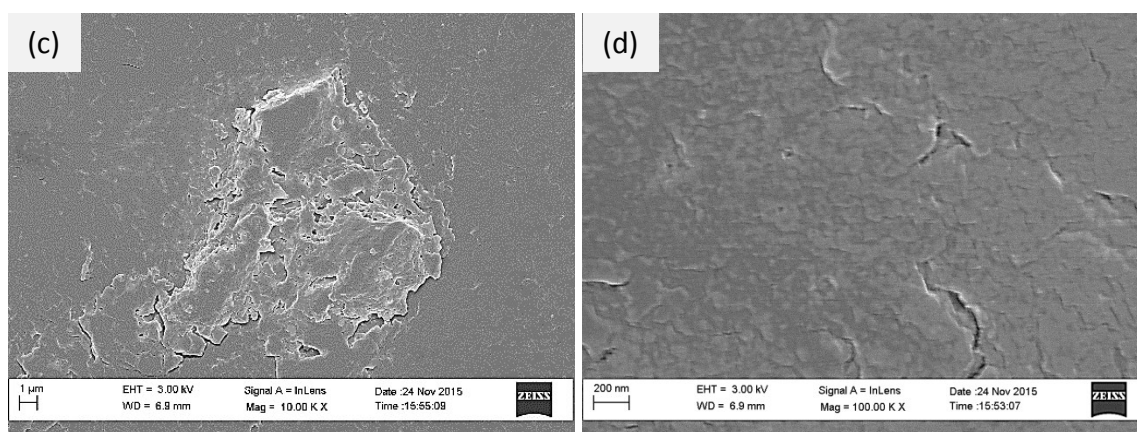


Figure 5.14 SEM images of a NIPS DMAc 0.3 mm PVDF membrane after the abrasion test for 2 weeks: (a) the cross-sectional overview; (b) a cross-sectional view close to the separation layer; (c) overview of the membrane surface; (d) high magnification image of the top separation layer

As shown in Figure 5.14, the NIPS DMAc 0.3 mm membrane was the least damaged sample among the NIPS samples after the abrasion test. The top layer remained almost unchanged after the test, but some debris can be seen on the surface. However, in high magnification SEM images, it is clear that intensive cracks start to appear on the membrane surface after the test, which would change the pore size and ruin the selectivity of the membrane.

Comparing all the CCD membrane and NIPS membranes after the accelerated abrasion test, the CCD Al/Al membrane could maintain its original pore structure, whereas NIPS membranes were severely damaged.

5.4.5 Comparison between the CCD and NIPS Methods

In conclusion, the difference between the NIPS and CCD methods for the production of flat sheet PVDF membranes are summarised in Table 5.6.

Table 5.6 Comparison between the NIPS and CCD methods for flat sheet PVDF membrane production

	NIPS	CCD
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Preparation method	The casting film of polymer solution together with the support is immersed in a coagulation bath composed of a non-solvent for the polymer. The polymer solution is then transformed from a liquid to a solid state due to the exchange of the solvent in the polymer solution with the non-solvent from the coagulation bath.	The casting film of the polymer solution is unidirectionally cooled from one side to a certain temperature far below the freezing point of the solvent. The solvent starts nucleation and crystallization, while the polymer precipitates to form the final membrane structure. Then the solvent is leached out by the iced water.
Typical structure	Asymmetric structure with a dense skin layer supported by finger-like voids and a sponge-like layer	A thin separation layer of numerous tortuous pores supported by gradually changed, fully opened, interconnected and self-organized micro-channels
Possible influencing factors during operation with a fixed composition of polymer solution	- Composition of the coagulation bath medium; - Original temperature of the polymer solution; - Temperature of the casting plate; - Coagulation bath temperature; - Evaporation time; - Ambient temperature and humidity; - Casting thickness; - Viscosity of the polymer solution and coagulation bath; - Density of the polymer solution and coagulation bath; - Other hydrodynamic factors (that influence interfacial instability) such as hydraulic pressure, the manner of immersing casting film into coagulation bath	- Cooling temperature; - Cooling rate - Casting thickness
Permeation flux	Very low	high
Pore size distribution	Broad	sharp

Transport resistance from support	High	Very low
Anti-fouling property	Poor	good
Anti-wearing property	Poor	good
Pore structure stability	Poor	excellent

5.5 Conclusions

In this work, we have compared the membrane structure, surface hydrophilicity, filtration performance and mechanical strength of the membranes prepared by the CCD and NIPS methods. The CCD membranes have shown excellent permeation performance and mechanical properties overwhelming the traditional NIPS membranes, and they are of great potential to upgrade the existing filtration units. The manufacturing process based on the proposed mechanism is of much less influencing factors compared to the conventional standard NIPS approach, and thus is highly reliable and repeatable. The principles can also be easily adapted to other commonly used membrane materials such as polyethersulfone and cellulose acetate, and it is expected to open up a new route for manufacturing other high-performance polymeric porous membranes.

5.6 References

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Chapter 6 Enhancement of CCD PVDF Membranes by Blending PEG

6.1 Abstract

Poly(vinylidene fluoride) (PVDF) membranes have been intensively studied, successfully commercialised and widely applied in various separation processes for years due to its outstanding inert material natures. Currently, PVDF membranes are mainly produced by the non-solvent induced phase separation (NIPS) method in both laboratory research and industrial manufacture. However, such NIPS membranes do have some structural drawbacks, and show poor performance and severe fouling in real applications due to the technique limits of the preparation method and the hydrophobic nature of the material. In Chapter 4, a novel combined solvent crystallisation and polymer diffusion (CCD) method has been established to produce high-performance PVDF membranes with a unique asymmetric structure. In this research, polyethylene glycol (PEG) was employed as a hydrophilic polymer additive to further enhance the performance of the CCD PVDF membranes. Comparisons were made on the membrane structure, performance and properties between the CCD PVDF/PEG blend membranes, the pure CCD PVDF membranes and some commercial membranes. It was found that the high permeation flux of the CCD membranes could be further enhanced by the addition of PEG while the pore size was even slightly reduced. In particular, the pure water flux of the PVDF A1/A1 membrane was almost doubled upon the PEG addition, and is significantly higher than that of the commercial PVDF UF membranes. The CCD PVDF/PEG blend membranes therefore have great potential to replace existing commercial membranes.

6.2 Introduction

PVDF membranes have attracted numerous investigations and been commercialised and widely applied in various kinds of separation processes for decades. That is because the PVDF material has several advantageous properties, such as hydrophobicity, thermal stability, chemical resistance and great mechanical strength [1-3]. Besides, PVDF can be dissolved in common organic solvents including *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), *N*-Methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO), making it possible to produce PVDF membranes via the phase separation technique [4, 5]. In fact, the phase separation techniques, particularly the NIPS method, dominate the preparation of PVDF microfiltration/ultrafiltration (MF/UF) membrane in both laboratories and industries [1, 6]. However, low water permeate flux and susceptibility to fouling are two inevitable issues

due to the hydrophobic material nature, especially when the PVDF membranes are applied in the treatment of wastewater containing oil and proteins. This has generated numerous research works aiming at increasing the membrane hydrophilicity while maintaining other properties. Two excellent review articles have been published on the hydrophilic modifications of PVDF membranes for water and wastewater treatment [1, 2].

Despite the poor membrane permeability and susceptibility to fouling caused by the material hydrophobicity, most PVDF membranes have structural defects caused by the preparation technique, i.e. the NIPS method. For example, the NIPS membranes normally have an asymmetric structure composed of a thin dense skin layer supported by finger-like voids and a sponge-like sublayer. The formation of macrovoids is often observed in the cross section of the membranes and will become mechanical weak points when membranes are applied in high-pressure treatments. Furthermore, the finger-like voids could be regarded as macrovoids with an organised and highly elongated shape [7]. On the other hand, the thin dense skin layer behaves as the separation layer and contributes to the membrane selectivity, but it always has low surface porosity, which is adverse to the membrane permeability. Moreover, the sponge-like structure is normally a cellular texture, which consists of open or closed pores. In the latter case, the trans-membrane resistance will be increased dramatically. These structural shortcomings could be improved by varying the membrane preparation conditions or applying the modification techniques [1, 2], but could not be completely solved. Most commercial PVDF membranes for industrial use possess pure water flux of only 200 litre per square meter per hour under 1 bar pressure difference (LMH bar^{-1}), and need to be cleaned frequently in order to remove the fouling layer and maintain the throughput of the membrane modules.

In Chapter 4, a new concept of membrane manufacturing technique by combining oriented green solvent crystallisation and polymer migration has been proposed, and asymmetric membranes with a considerably porous dense separation layer and gradually opened micro-channels have been produced. Compared to the conventional NIPS technique, the newly developed CCD technique has shown several advantages. For example, the CCD method employs DMSO as the solvent. In the industrial manufacturing processes of PVDF membranes via phase inversion technique, DMAc is one of the most commonly used as it helps to control the formation of finger-like structure and defects in the membranes [8]. However, it is a harmful chemical, and many developed countries including EU and Singapore have started thinking of restricting its use [9, 10]. Contrarily, DMSO is also a good solvent to PVDF and is non-hazardous according to the US Food and Drug Administration and other applicable

regulations, making it a potential replacement of DMAc in the industrial production of PVDF membranes.

Regarding the unique structure of the CCD PVDF membranes, the thin separation layer is composed of a number of tortuous pores, which presents as intensively scattered porous on the membrane surface facilitating the high permeance of the membranes. The porous separation layer is supported by numerous well-arranged micro-channels whose size gradually increases from the separation layer. The micro-channels are full-opened and interconnected, which actually give negligible resistance to the water permeation. As a result, the CCD PVDF membranes have shown excellent filtration performance with pure water flux 100 times higher than those NIPS membranes with similar pore size. Besides, the CCD membranes also possess great mechanical properties overwhelming the traditional NIPS membranes. All these findings demonstrate the potential of upgrading the existing filtration units with the high-performance PVDF membranes prepared by the CCD technique.

However, commercial PVDF membranes are normally prepared with modified PVDF to improve permeation characteristics. Thus, using modified PVDF in the CCD method is expected to further improve the CCD membranes. Polyethylene glycol (PEG) is a well-known hydrophilic polymer and has been used to improve the performance of PVDF membranes successfully [11-13]. When PEG is blended with PVDF, it enhances the hydrophilicity of the membrane material, and the water permeation flux can then be considerably improved [12]. In this work, CCD PVDF/PEG blend membranes were prepared to make further enhancement on the pure membranes obtained in our previous work, therefore. The prepared membranes were subjected to a series of characterisations including scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), X-ray diffraction (XRD) analysis, water contact angle measurement, pure water filtration test and tensile test. The effects of blending PEG on the membrane morphology, PVDF crystal structure, surface hydrophilicity, filtration performance and mechanical properties were investigated.

6.3 Methodology

6.3.1 Materials

Commercial PVDF (Kynar[®] K-761, $M_w = 440,000$ Da, $\rho = 1.79$ g/cm³) was purchased from Elf Atochem and was dried at 80 °C for 24 hours before use. PEG 400 ($M_n = 400$), bovine serum albumin (BSA) and DMSO were purchased from Sigma-Aldrich, UK and were used as received.

6.3.2 Membrane Preparation

PVDF/PEG blend flat sheet membranes with highly asymmetric and self-assembled ordered structure were produced by the CCD method, which has been introduced in details in the previous chapters. The PVDF dope solutions were prepared by dissolving PVDF and PEG 400 in DMSO with the PEG : PVDF : DMSO mass ratio of 1 : 4 : 16 at 80 °C, and then was left in the oven at 80 °C overnight to remove bubbles. The dope solution was then cast of a certain thickness on a casting plate, followed by unidirectional cooling to a pre-determined temperature, which is achieved by contacting with a pre-cooled cold plate. The material of the cold and casting plates was aluminium or glass to realise different thermal conductions and thus different cooling rates. After complete quenching, the frozen casting film was immersed in iced water to leach the solvent out. The water was changed regularly to remove the residual solvent. Apart from the materials of the plates, the casting thickness was varied in order to investigate its effects on the membrane morphology and properties.

For the fouling study, a control sample of PVDF membrane with the casting thickness of 0.3mm was fabricated by the conventional NIPS method using deionised water as the non-solvent. The same polymer dope solution was cast on a glass plate at room temperature and was then immediately immersed into the water bath. The obtained membrane was then in deionised water, which was changed frequently to remove the residual solvent before all the characterisations. The preparation conditions of each sample were summarised in Table 6.1.

Table 6.1 Casting conditions for the preparation of flat sheet membranes

Sample		Solvent	Casting Thickness	Casting Plate	Cold plate/ Cooling Condition
CCD	G/G*	DMSO	1 mm	6 mm Glass	6 mm Glass plate (-30 °C)
	Al/G	DMSO	1 mm	6 mm Al	6 mm Al plate (-30 °C)
	Al/Al 1.0mm	DMSO	1 mm	6 mm Al	6 mm Al plate (-30 °C)
	Al/Al 0.3mm	DMSO	0.3 mm	6 mm Al	6 mm Al plate (-30 °C)
NIPS	DMSO 0.3mm	DMSO	0.3 mm	6 mm Glass	N/A

*: material of the casting plate/material of the cooling plate, G represents glass and Al stands for aluminium.

6.3.3 Membrane Characterisations

The wet membranes were used directly for filtration tests, gas-liquid displacement porosimetry and the abrasion test, but were dried via solvent (ethanol) exchange technique prior

to other characterizations. All the characterisation methods including SEM, FTIR, DSC, XRD, water contact angle measurement, pure water permeation test, BSA fouling test, gas-liquid displacement porosimetry and mechanical test have been described in Section 5.3.3.

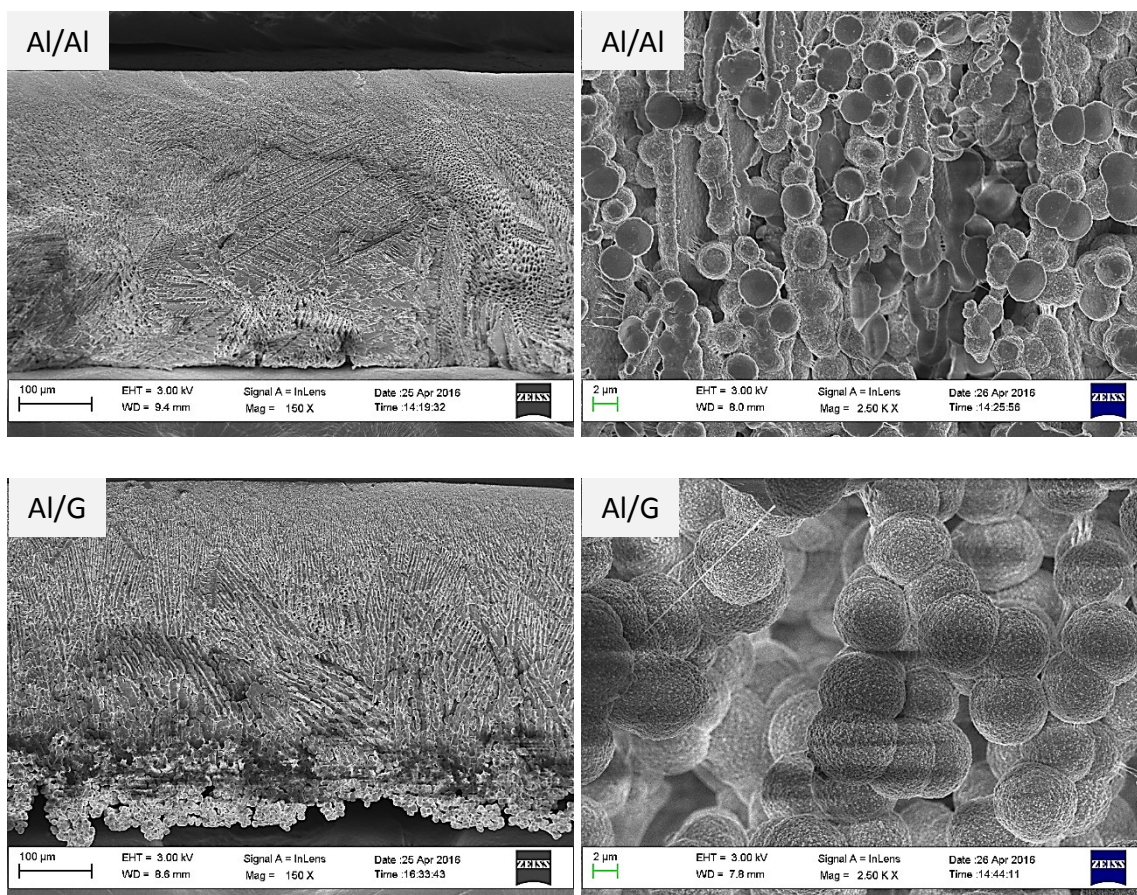
6.4 Results and Discussions

In this section, the effects of blending PEG in PVDF dope solution on the membrane morphologies, PVDF crystal phase, surface hydrophilicity, filtration performance and mechanical strength will be discussed in details.

6.4.1 Membrane Structure

6.4.1.1 Morphological Structure

The morphological structure including separation layer, cross section and supporting layer of the PVDF/PEG blend membranes prepared by the CCD method under different cooling rates was investigated by SEM.



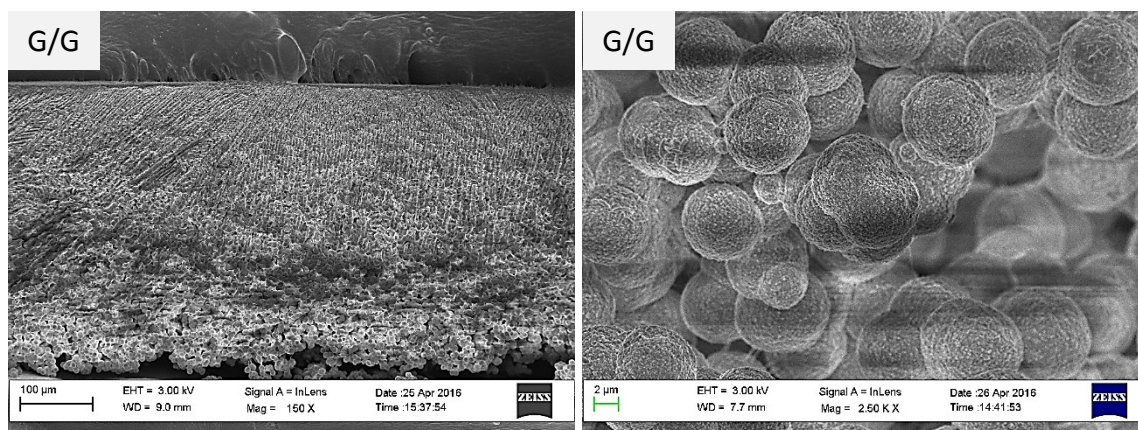
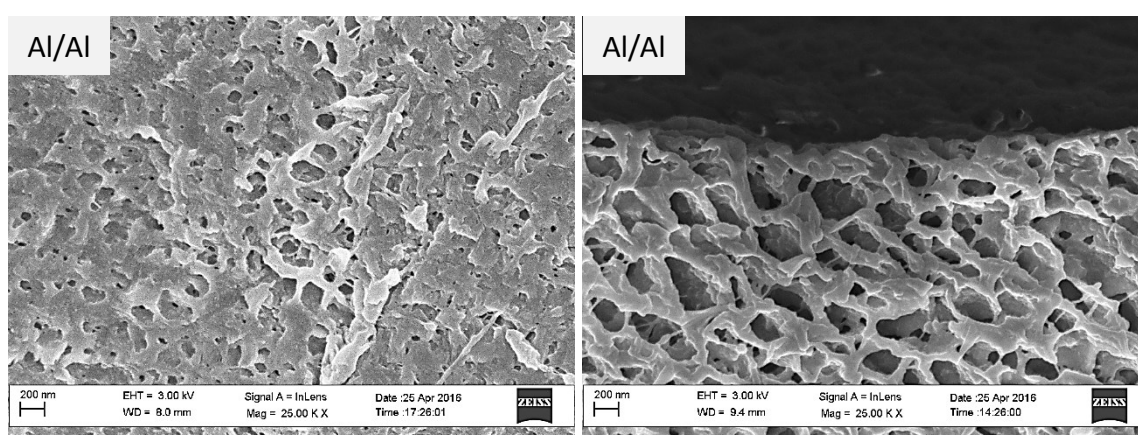


Figure 6.1 SEM images of (left) cross-sectional overview and (right) back surface of the supporting layer of the CCD PVDF/PEG blend membranes prepared by using different combinations of casting plate and cooling plate

Similar to the pure PVDF membranes prepared by the CCD method (Section 4.5.1 and Section 5.4.3.1), all the CCD PVDF/PEG blend membranes have an asymmetric structure composed of a considerably porous dense separation layer supported by numerous well-oriented gradually opened micro-channels (Figure 6.1 and Figure 6.2). When glass plate was employed in the membrane preparation process, the formation of large PVDF spherulites was clearly observed in the supporting layer, especially at the back surface (Figure 6.1). This could be attributed to the slow cooling rate due to the use of the glass plate, which would lead to a less steep temperature gradient in the polymer film and thus slower polymer diffusion. Both factors would contribute to the growth of PVDF spherulites in the late stage of the freezing process.



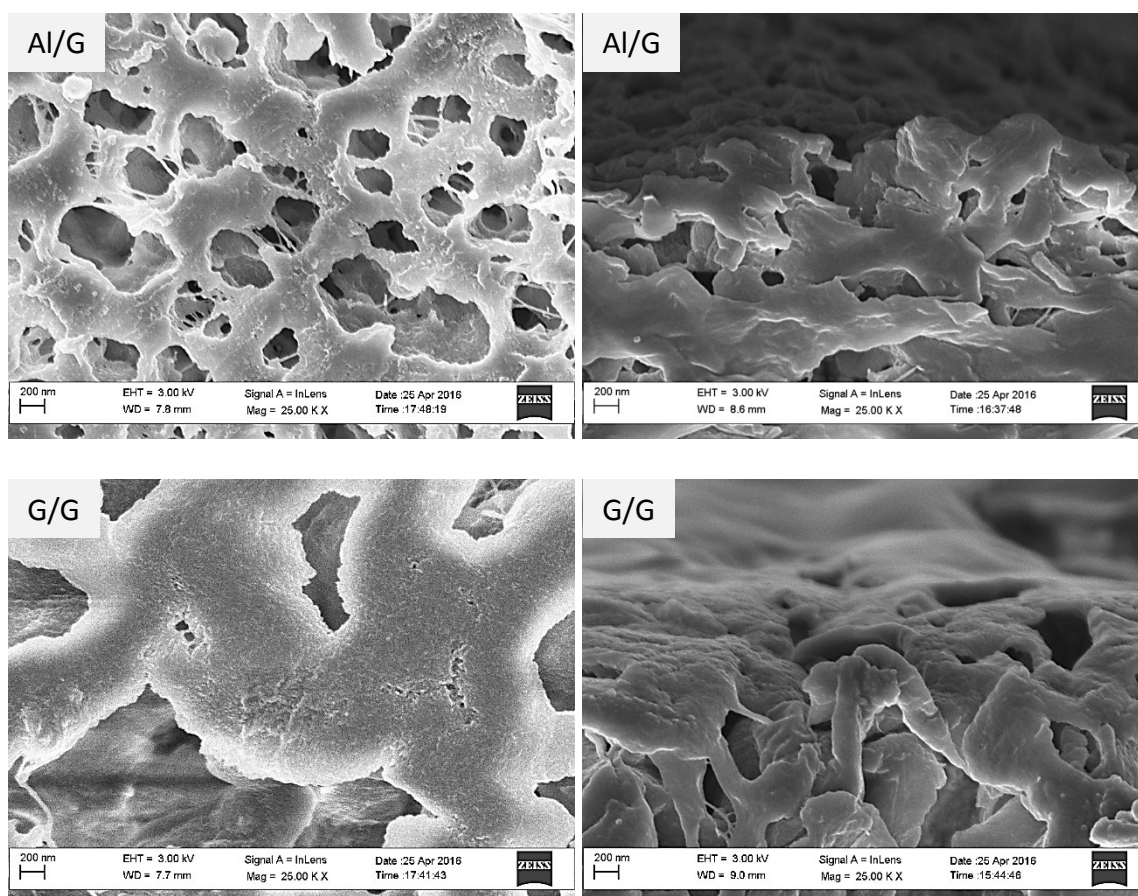


Figure 6.2 SEM images of (left) surface morphology and (right) close cross-sectional view of the separation layers of the CCD PVDF/PEG blend membranes prepared by using different combinations of casting plate and cooling plate

According to the proposed mechanism of the CCD method (Section 4.5.1), the slow cooling rates and polymer diffusion in the Al/G and G/G cases would have produced bigger initial DMSO crystals than in the Al/Al case. This agrees well with the SEM images shown in Figure 6.2.

6.4.1.2 Pore Structure

Table 6.2 Permeation characteristics and water contact angle of PVDF/PEG membranes prepared by CCD method compared with pure CCD PVDF membranes and some commercial PVDF membranes

Membrane Type		Pure water flux (LMH bar ⁻¹)	Pore size (nm)	Water contact angle (°)
CCD membranes*	PVDF G/G	10998 ± 407	345 ± 26	99.5 ± 4.8
	PVDF Al/G	5017 ± 547	119 ± 10	93.4 ± 1.6
	PVDF Al/Al	861 ± 78	45 ± 3	89.5 ± 3.5

	PVDF/PEG G/G	12942 ± 355	308 ± 30	82.0 ± 2.7
	PVDF/PEG Al/G	7552 ± 803	95 ± 10	98.0 ± 1.7
	PVDF/PEG Al/Al	1711 ± 155	36 ± 2	82.6 ± 3.7
Commercial membranes**	DOW	40 - 120	30	Modified hydrophilic PVDF
	EVOQUA	20	40	
	KOCH PURON®	100	30	
	GE ZeeWeed 1500	135	20	
	TORAY	30 (MBR)	80	
	Pall	> 3000	200	
	Pall	> 8200	450	
	TriSep TM10	90	200	
	Hydranautics HYDRAcap®	34 - 110	80	

*: Samples are named based on the polymers in the dope and the combination of casting plate and cooling plate in the CCD process; data of pure CCD PVDF membranes were obtained from previous work.

**: Pore sizes are nominal pore sizes provided by the manufacturer, while flux was converted from product brochure of membrane modules, but operation pressure and other conditions are unclear.

The pore sizes of the CCD PVDF/PEG blend membranes were evaluated by the bubble point method and are compared to the pure CCD PVDF membranes, as summarised in Table 6.2. Figure 6.3 shows the typical pore size distribution of the CCD PVDF/PEG blend membranes. Similar to the pure CCD PVDF membranes, the PEG blended membranes all have a sharp pore size distribution. Figure 6.3 (a) shows an Al/Al 1.0mm sample, which has a sharp peak at 37.45 nm with a percent flow of 67.75%; Figure 6.3 (b) shows an Al/G 1.0mm sample, which has a sharp peak at 97.95 nm with a percent flow of 94.48%; and Figure 6.3 (c) shows a sharp peak at 287.6 nm with a percent flow of 92.21%.

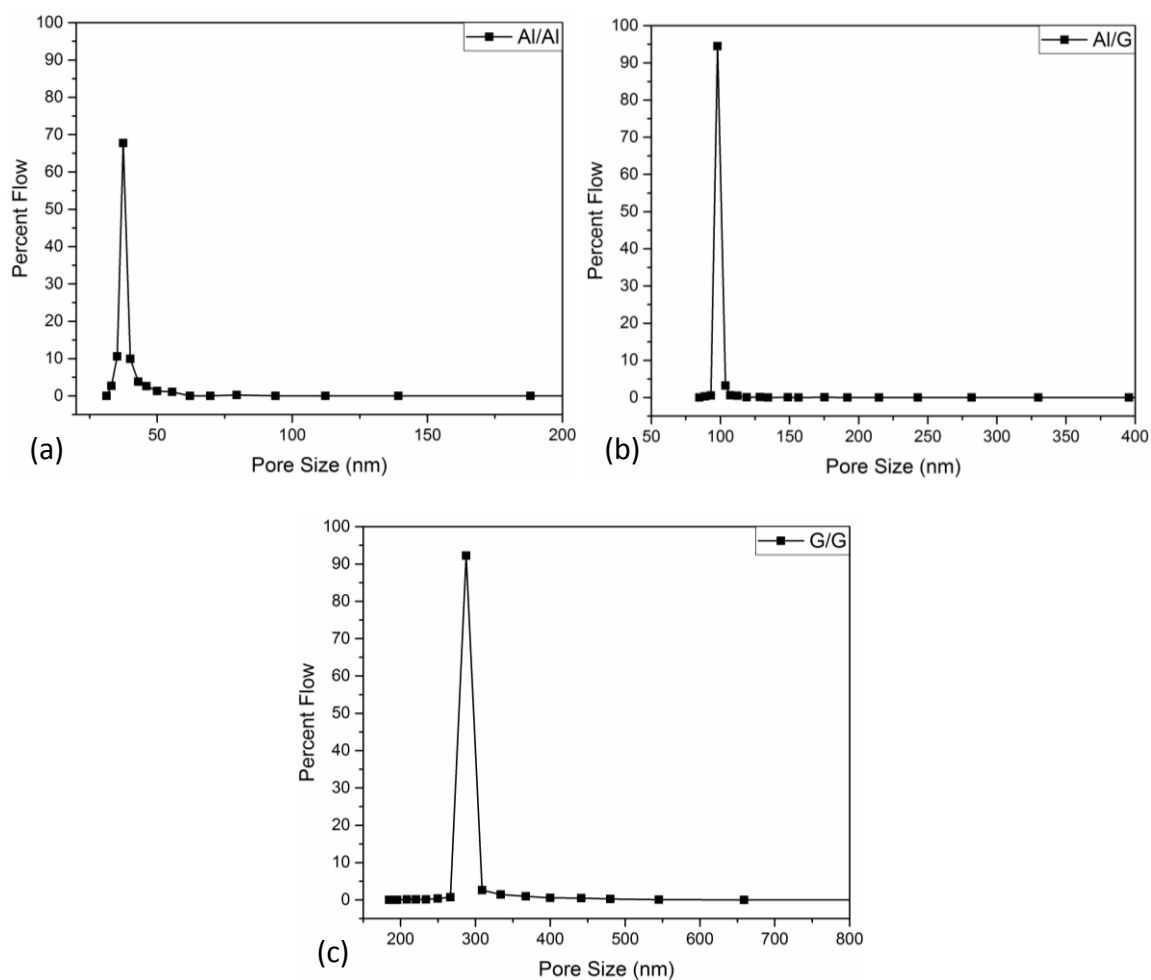


Figure 6.3 Pore size distribution of the CCD PVDF/PEG blend membranes measured by the gas-liquid displacement method: (a) CCD Al/Al 1.0mm sample; (b) CCD Al/G 1.0mm sample; (c) CCD G/G 1.0mm sample

6.4.1.3 Crystal Structure

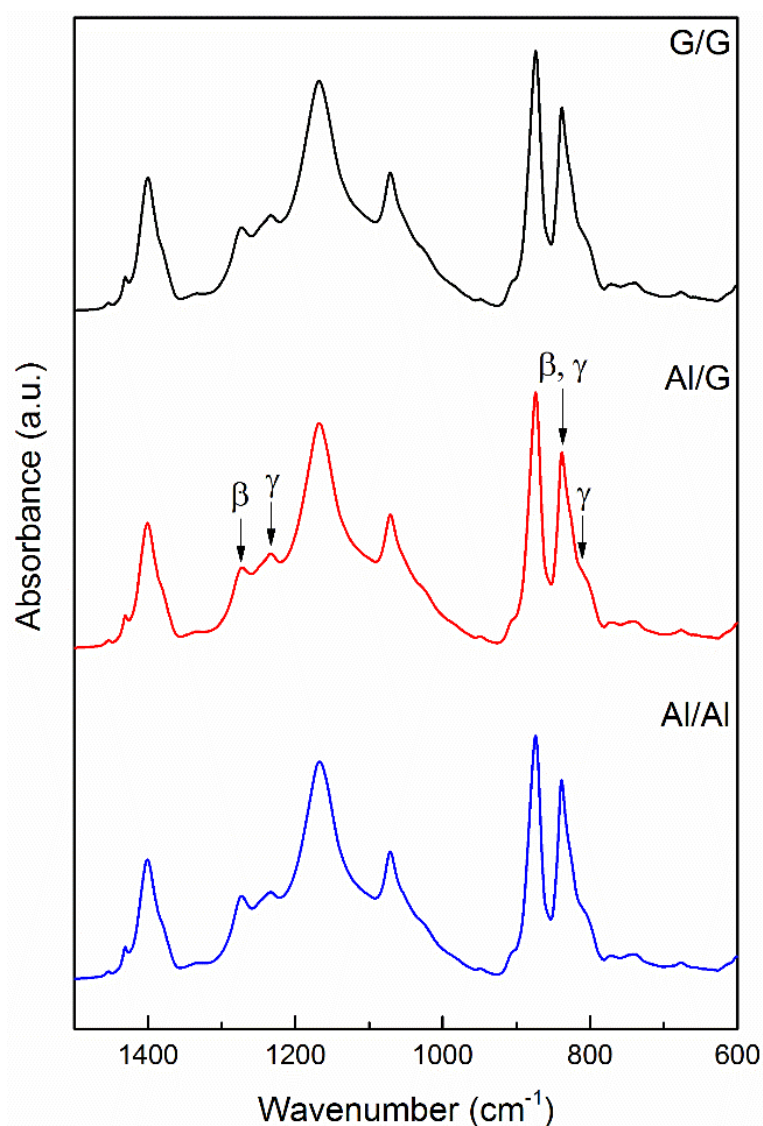


Figure 6.4 FTIR spectra of the CCD PVDF/PEG blend membranes

The PVDF crystal structure in the CCD PVDF/PEG blend membranes were studied by FTIR, XRD and DSC. Compared to the FTIR spectra and XRD patterns of the pure CCD PVDF membranes, no obvious changes were observed upon the PEG addition. As shown in Figure 6.4, the bands at 840 and 1275 cm^{-1} are the characteristic of β phase absorption and γ phase can be well identified from the peaks at 811, 840 and 1233 cm^{-1} . It can be seen that the blend membranes show the intensive peaks of only β and γ phase crystallites.

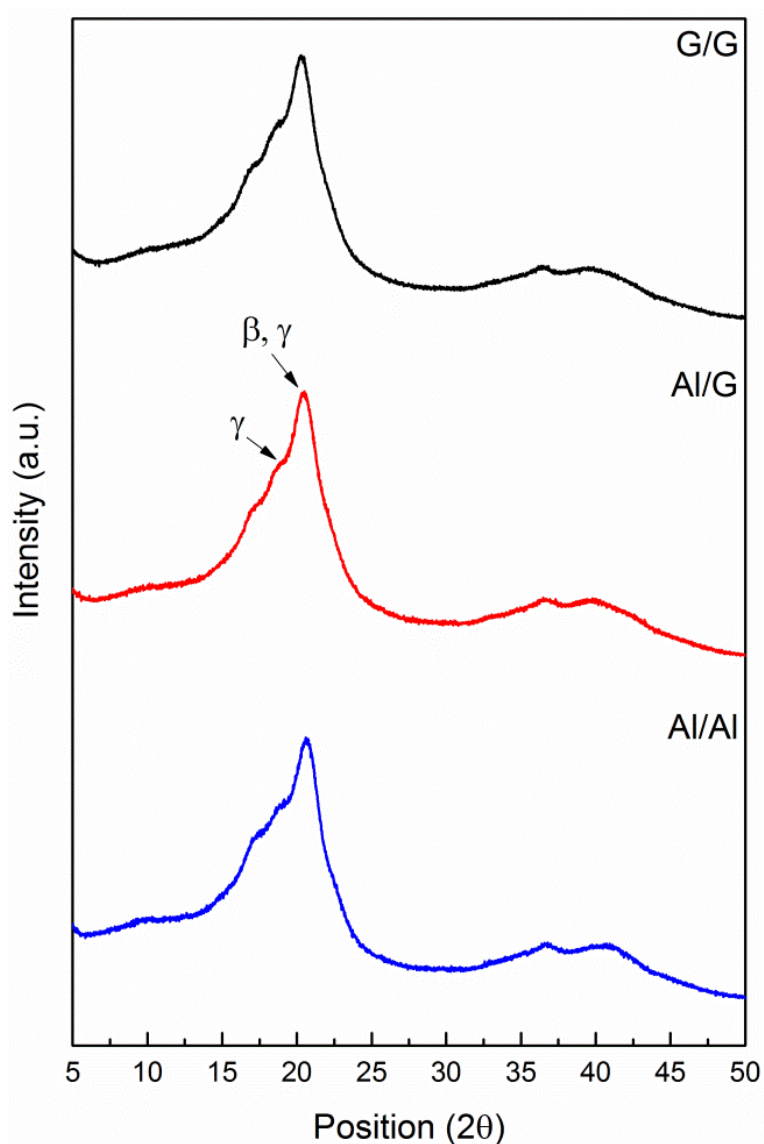


Figure 6.5 XRD patterns of the CCD PVDF/PEG blend membranes.

Similar conclusions could be drawn from the XRD analysis that the CCD membranes are composed of mainly β phase (the sharp diffraction peak at 20.3°) and also γ phase PVDF crystallites (peaks at 18.8° and 20.3°), as shown in Figure 6.5. The crystallinity of PVDF in the blend membranes was also evaluated by DSC and were increased to about 65% for all CCD membranes excluding PEG (Figure 6.6), which is just slightly higher than the pure PVDF CCD membranes.

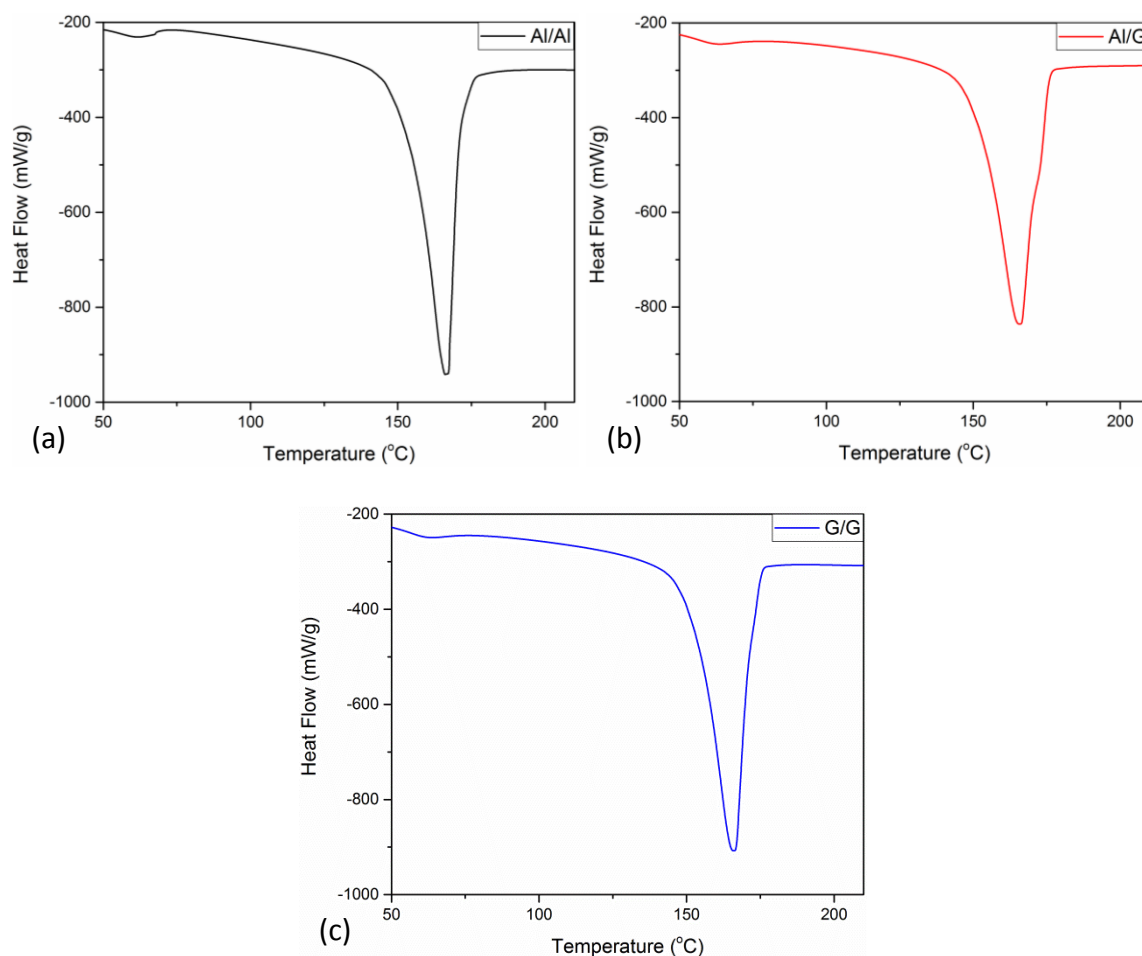


Figure 6.6 DSC results of the CCD PVDF/PEG blend membranes: (a) Al/Al 1.0 mm, crystallinity 64%; (b) Al/G 1.0 mm, crystallinity 66%; (c) G/G 1.0 mm, crystallinity 64%

6.4.2 Membrane hydrophilicity

As known to all, improving surface hydrophilicity is often considered as an effective approach capable of enhancing the water permeation of membranes [1, 2]. However, in this work, the results indicated that the water contact angle was almost unaffected by blending PEG in the dope solution (Table 6.2). In the Al/Al case and G/G case, the water contact angles of the PVDF/PEG blend membrane were smaller than the pure CCD PVDF membranes, which means that the membrane hydrophilicity was slightly increased. On the other hand, the contact angle was slight increased by the PEG addition in Al/G case. It should be noted that the water contact angle data only stand for the membrane surface wettability, which is affected by the exact properties of the water droplet and the membrane such as surface roughness. The results therefore could not represent the hydrophilicity of pore walls inside the membrane, which would influence the membrane permeance significantly.

6.4.3 Filtration Performance

The results of the CCD PVDF/PEG blend membranes and pure CCD PVDF membranes in the pure water permeation test were summarised in Table 6.2, and were also compared to some commercial PVDF membranes. Apparently, the permeation flux of the pure CCD PVDF membranes could be further enhanced by simply blending the hydrophilic polymer additive PEG in the dope solution, which is in agreement with previous studies [12]. Particularly, significant improvement was observed for the Al/Al UF membrane, whose pure water flux was increased from 861 ± 78 LMH bar⁻¹ to 1711 ± 155 LMH bar⁻¹ after modification, whilst the pore size was even slightly decreased from 45 ± 3 nm to 36 ± 2 nm. On the other hand, for the Al/G and G/G cases, the membranes are within the microfiltration range and have large pore sizes. As a result, the enhancement on the membrane permeance caused by the improved membrane hydrophilicity is not significant.

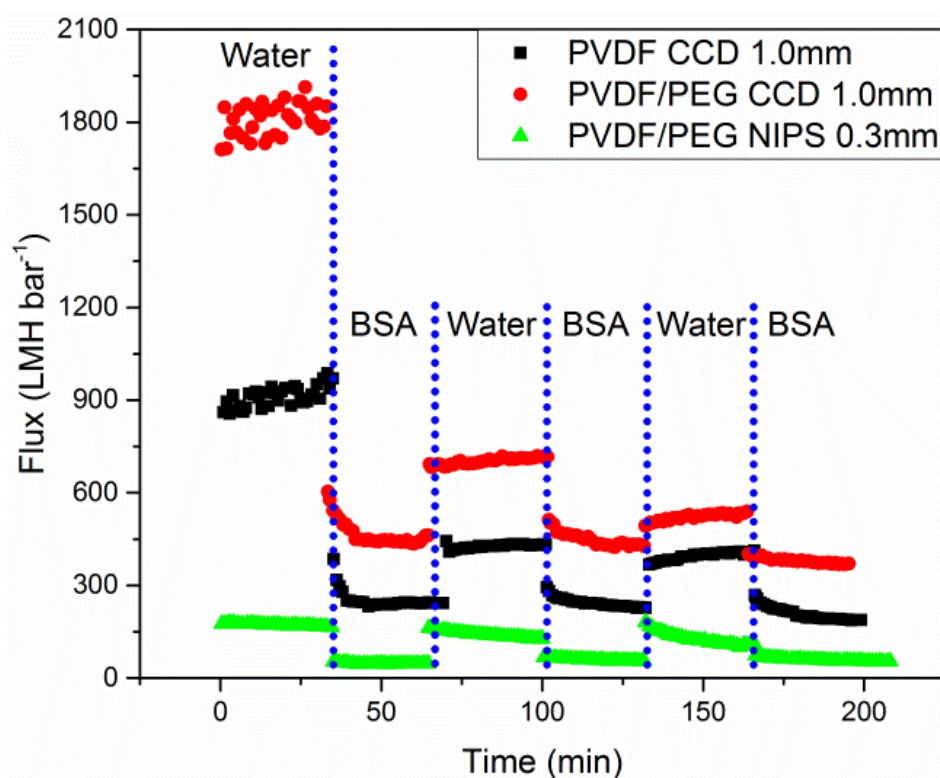


Figure 6.7 Permeation flux of pure CCD PVDF Al/Al 1.0 mm membrane (black), CCD PVDF/PEG Al/Al 1.0mm blend membrane (red) and NIPS PVDF/PEG 0.3mm blend membrane in the three cycles of pure water/BSA solution fouling test

As being recommended by most commercial membrane suppliers, UF/MF membrane modules should be periodically cleaned with an interval of 30-40 minutes after operation to resume permeability. Thus, the fouling test was conducted involving three cycles of pure water and 1.0 g/L BSA solution, and the flux recovery of three different membranes after cleaning

was tested. As shown in Figure 6.7, both the pure water fluxes of the CCD PVDF membranes prepared with or without PEG addition could not be fully recovered after fouling with BSA, which is in agreement with other PVDF membranes prepared by the phase inversion methods [14-17]. Nevertheless, even after fouling, both CCD membranes showed superior permeation flux compared to the conventional NIPS membrane. Moreover, the BSA flux of the CCD PVDF/PEG blend membrane was around 400 LMH bar⁻¹, which was about two times of the pure CCD PVDF membrane (around 200 LMH bar⁻¹). Considering the initial pure water flux of the blend membrane, which is almost doubled compared with the pure PVDF membrane, it seems that the addition of PEG did not improve the fouling resistance of the CCD membrane. This might be attributed to the unchanged membrane surface hydrophilicity (Section 6.4.2), which means that the high affinity of PVDF membrane to BSA protein was nearly unaffected by blending PEG. It was still difficult to remove the BSA fouling layer from the membrane surface, therefore.

Table 6.3 Static adsorption fouling test results of the CCD and NIPS membranes

Sample	CCD Al/Al PVDF	CCD Al/Al PVDF/PEG	NIPS PVDF/PEG
BSA Adsorption (mg/g)	16.01 ± 0.20	21.87 ± 0.61	27.75 ± 1.62

Both of the 0.3 mm thick CCD and NIPS blend membranes were subjected to the static adsorption fouling test. As listed in Table 6.3, all the three membranes showed high BSA adsorption, which is probably due to the use of DMSO as the solvent (Section 5.4.1). It was found that the CCD PVDF/PEG blend membrane showed even higher adsorption than the unmodified CCD PVDF membrane. However, both CCD membranes showed lower BSA adsorption than the conventional NIPS membrane, which is contrary to the static fouling test results of pure CCD and NIPS PVDF membranes studied in Section 5.4.1. However, it should be noted that the change in the accessible surface area varied with samples, and would affect the BSA adsorption results significantly. The result should not be over interpreted, therefore.

6.4.4 Mechanical Strength

Table 6.4 Tensile test results of CCD PVDF/PEG membranes compared with pure CCD PVDF membranes

Sample	Maximum Load (N)	Elongation at Maximum Load (%)	Tensile Stress (MPa)	Young's Modulus (MPa)	Maximum Water Speed* (m/s)
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PVDF Al/Al	12.0 ± 3.0	47.8 ± 5.9	2.4 ± 0.6	68.1 ± 12.8	23.6
PVDF Al/G	9.0 ± 2.8	26.3 ± 4.9	1.9 ± 0.6	75.2 ± 13.1	20.1
PVDF G/G	8.0 ± 0.8	16.4 ± 6.8	1.9 ± 0.2	66.5 ± 9.2	18.8
PVDF/PEG Al/Al	6.9 ± 0.3	15.1 ± 2.2	1.7 ± 0.1	72.6 ± 7.5	17.3
PVDF/PEG Al/G	7.6 ± 0.7	12.9 ± 3.6	1.6 ± 0.1	72.0 ± 4.7	18.3
PVDF/PEG G/G	4.9 ± 0.3	12.3 ± 3.0	1.3 ± 0.1	57.4 ± 8.0	14.4

*: Maximum water speed was calculated based on a flat-sheet membrane of dimensions $1 \times 2 \text{ m}^2$ (width $\times$ length), water flows along the length direction.

Table 6.4 compares the mechanical properties of the pure CCD PVDF membranes and blend PVDF/PEG membranes. Similarly, with a faster cooling rate used during the membrane fabrication process, the PVDF/PEG blend membrane shows better mechanical properties in terms of higher fracture load, longer elongation and higher tensile stress, which was probably due to the microstructural change in the membrane depending on different cooling rates. For example, the membranes with smaller micro-channels but in larger quantities will be produced with a faster cooling rate. When the membrane was subjected to the tension, the existence of smaller but more micro-channels would facilitate the distribution of stress in the membrane and the energy dissipation by deformation. Thus, the failure of the membrane would be postponed.

Furthermore, the maximum water speed for each sample was also calculated and the results are summarised in Table 6.4. It could be seen that the maximum water speeds of the blend membranes are smaller than those of the pure membranes due to the addition of PEG. However, even for the worse case of the PVDF/PEG G/G membrane, such a membrane of dimensions $1 \times 2 \text{ m}^2$ (width $\times$ length) is able to withstand the drag force generated from the flowing water along the length direction with a speed of 14.4 m s^{-1} . It is much higher than the practical flow speeds used in real applications (normally less than 6 m s^{-1}). This means that the CCD PVDF/PEG blend membranes would not only show excellent filtration performance, but also have longer life span compared to the commercial PVDF membranes.

6.5 Conclusion

In this research, PEG 400 was adopted as a hydrophilic polymer additive to modify PVDF membranes prepared by the CCD method. The presence of PEG in the system did not

affect the formation mechanism of the membranes during the CDD process. As a result, similar to the pure CCD PVDF membranes, the modified membranes have an asymmetric structure with porous separation layer supported by gradually opened micro-channels, and they are also composed of PVDF β phase and γ phase crystallites. The pure water flux of the membranes was further improved by adding PEG as expected, while the mean flow pore size was found to be slightly reduced. However, the mechanical properties of the CCD membranes were decreased by the introduction of PEG, although they are still much higher than those of the commercial NIPS membranes. Since the CCD method is a newly developed technique and there are still many questions to be answered, more research work should be done in the future to reveal the reasons for the effects of PEG addition, such as on the PVDF crystallinity and membrane mechanical properties.

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Chapter 7 Conclusions and Recommendations for Future Work

7.1 Conclusions

In this study, flat sheet poly(vinylidene fluoride) PVDF membranes have been reinforced by blending palygorskite (PGS) in the dope solution, followed by the phase inversion process. The abrasion resistance of the reinforced membranes was assessed by a proposed convenient quantitative method and has shown significant improvement. The permeability of the reinforced membranes was also increased considerably compared with the unreinforced membranes, but still not breaking the bound of the PVDF membranes prepared via the phase inversion methods.

A new concept for membrane fabrication by combining solvent crystallisation and polymer diffusion (CCD) has therefore been established. In this method, the crystallites of the solvent serve as pore templates, and polymer diffusion occurs at the same time of solvent crystallisation to constrain the agglomeration of solvent crystallites. Thus, the pore size in the final membrane can be easily controlled to the ultrafiltration range. Asymmetric membranes with a unique structure have been produced by the proposed CCD method and different pore sizes ranging from MF to UF were achieved by applying different cooling rates. Compared to PVDF membrane prepared by traditional non-solvent induced phase separation (NIPS) method, the membranes prepared by the newly developed CCD method have shown superior filtration performance with permeation flux substantially higher than commercial membranes with similar pore sizes, and very high stable permeation flux after fouling. The CCD membranes also possess excellent mechanical properties such as high-pressure load and high resistance to abrasion. Furthermore, the filtration flux of the CCD PVDF membranes can be further improved by adding PEG to the dope solution.

Following sections summarise the main conclusions of individual work that has been covered in this thesis.

7.1.1 Preparation of PVDF/PGS Composite Membranes with Enhanced Abrasion Resistance

Membrane wearing is one of the important issues that membranes normally encounter in the application of wastewater treatment. In this study, reinforced PVDF flat sheet membranes

have been prepared by a combination of NIPS and thermally induced phase separation (TIPS) methods from dope solutions containing varied amounts of PGS. The produced membranes have been subjected to a series of standard membrane characterisation tests as well as a specifically developed abrasion test, using which the abrasion resistance of a flat sheet membrane can be investigated quantitatively. The experimental results reveal that the blending of PGS lead to the formation of more PVDF crystallites with smaller size, and enhanced the membrane mechanical strength and permeability without compromising its selectivity. In addition, a dramatic increase of the membrane abrasion resistance has been observed when the PGS loading amount reached 10 wt.%, which could be attributed to the transition of abrasion mechanism from a ductile manner to a brittle manner.

7.1.2 Preparation and Characterisation of PVDF Membranes Prepared by the CCD Technique

In this study, a new membrane preparation technique has been proposed based on a combination of solvent crystallisation and polymer diffusion. The mechanism of membrane formation process has been also studied and explained based on unidirectional solvent crystallisation, polymer diffusion and precipitation during the quenching process, followed by solvent leaching and formation of the pores and channels. PVDF has been employed as a benchmark membrane material to prepare flat sheet membranes via the CCD method. The effects of different cooling conditions, casting thickness and choice of solvent on the membrane formation process, the final membrane structure and performance have been investigated. It has been found that the membrane structure is significantly affected by the cooling rate, as it influences the rates of solvent crystallisation and polymer migration. The ultimate membrane structure is also dramatically influenced by the solvent nature since it decides the sequence of solvent crystallisation and polymer phase separation during the freezing process.

Moreover, membrane samples have been prepared using the conventional NIPS method from the same dope solutions for comparison. The differences between the CCD membranes and the NIPS membranes have been compared in terms of membrane structure, crystal phase, surface hydrophilicity, filtration performance, mechanical strength and abrasion resistance. The characterisation results indicate that the CCD membranes display excellent pure water flux (two orders of magnitude higher) and much higher steady flux after BSA fouling than the conventional NIPS PVDF membranes. Besides, the CCD membranes also have superior

mechanical strength in terms of high-pressure load and better abrasion resistance compared to the NIPS membranes.

7.1.3 Further Enhancement of the CCD PVDF Membranes by Blending PEG

The performance of the PVDF flat sheet membranes prepared by the CCD method can be further enhanced by blending PEG into the dope solution. The experimental results suggest that the introduction of PEG has little influence on the membrane formation process and typical CCD structure can be observed in the resultant membranes. In particular, when high cooling rate (Al/Al case) was adopted, the pure water flux of the PEG blended membrane was nearly two times of the pure PVDF membrane due to the enhanced hydrophilicity of the membrane material. Meanwhile, the membrane pore size was even slightly reduced. Although the addition of PEG decreases the membrane mechanical strength, it is still much higher than that of the commercial NIPS membranes.

7.2 Recommendations for Future Work

7.2.1 Fundamental Study of the CCD Process

It has been demonstrated that high-performance PVDF membranes can be produced via the CCD method. Preliminary study on the membrane formation mechanism has been conducted including the effects of cooling conditions, solvent nature and casting conditions such as casting thickness. As the proposed CCD technique is newly developed, it is suggested that further study should be focused on the understanding of basic aspects of the CCD membrane formation process. For example, it would be beneficial to investigate the effect of PVDF polymers with different molecular weights on the diffusivity of polymer and hence polymer diffusion and precipitation in the freezing process. Besides, more combinations of casting plate and cooling plate with different materials and thicknesses could be employed to conduct a more detailed systematic study and it would be helpful to understand the freezing process. It would also be useful to study the effects of additives on the membrane formation process and hence the resultant membrane properties.

7.2.2 Continuous Production of the PVDF Flat Sheet Membranes by the CCD Method

PVDF flat sheet membranes have been prepared by bench casting followed by the CCD process in this study. It would be helpful to develop a system to produce PVDF flat sheet

membranes continuously. In a normal continuous membrane casting system, a belt is employed to transfer the polymer casting film from the casting knife to the coagulation bath continuously. In the continuous CCD process, a freezing chamber or plate is needed to provide unidirectional cooling. Thus, the design problem lies on the effective control of freezing direction since the polymer film is moving during the continuous casting process.

7.2.3 PVDF Hollow Fibre Membranes Prepared by CCD Method

Since the developed CCD method has been successfully used to prepare PVDF flat sheet membranes, it would be useful to apply this method in the fabrication of PVDF hollow fibre membranes. The main problem is to add the quenching set-up into the spinning set-up between the spinneret and the coagulation bath. A dual-layer spinneret with a solvent immiscible with the dope solution (e.g. hexane) flowing through the needle in the centre and the outer layer may be used. Then the temperature gradient across the membrane can be achieved by keeping one of two solvent flows at low temperatures. However, the recycle of the immiscible solvent will be another problem to be solved.

7.2.4 Preparation of Other Membranes by the CCD Method

In this work, PVDF has been used as a benchmark to investigate the feasibility of preparing high-performance polymeric membranes with unique asymmetric structure and superior mechanical strength via the newly developed CCD method. This technique should be implemented by preparing membranes from other materials, such as polyethersulfone and cellulose acetate, which both are commonly used polymeric membrane materials and can be dissolved in DMSO. Preparation of these membranes would be useful for providing a route to the commercialisation of the CCD technique.

List of Publications

Journal Publications

J. Ji, F. Liu, N. A. Hashim, M. R. M. Abed and K. Li, *Poly(vinylidene fluoride) (PVDF) membranes for fluid separation*. Reactive and Functional Polymers, 2015. **86**: p. 134-153.

J. Ji, S. Y. Zhou, C. Y. Lai, B. Wang and K. Li, *PVDF/palygorskite composite ultrafiltration membranes with enhanced abrasion resistance and flux*. Journal of Membrane Science, 2015. **495**: p. 91-100.

B. Wang, **J. Ji** and K. Li, *Crystal Nuclei Templated Nanostructured Membranes Prepared by Solvent Crystallisation and Polymer Migration*. Nature Communications, 2016. **7**.

Patents

J. Ji, B. Wang and K. Li, Separation Membranes (patent application number 1606988.2), filed on 21th April 2016.

Conference Presentations

J. Ji, S.Y. Zhou and K. Li, *PVDF/Palygorskite Composite Membranes for Wastewater Treatment*. International Congress on Membrane and Membrane Processes (ICOM – 2014), Suzhou, P. R. China (oral).

J. Ji, B. Wang and K. Li, *Morphology and Performance of PVDF Hollow Fibre Ultrafiltration Membranes Using DMSO as the Solvent*. Euromembrane 2015, Aachen, Germany (poster).

Appendix

Permissions summary table for third party copyright works

Page No.	Type of Work	Name of Work	Source of Work	Copyright holder and contact	Permission requested on	I have permission: yes/no	Permission license No.
28	figure	Fig. 1. A schematic representation of a binary phase diagram of a polymer solution showing a liquid-liquid demixing gap...	vandeWitte, P., et al., <i>Phase separation processes in polymer solutions in relation to membrane formation</i> . Journal of Membrane Science, 1996. 117 (1-2): p. 1-31.	© 2016 Elsevier B.V.	28/07/2016	yes	3917640530745
35	figure	Figure 7 Ternary phase diagram polymer-solvent-non- solvent with directions of distinguished “composition paths”...	Stropanik, C., L. Germic, and B. Zerjal, <i>Morphology variety and formation mechanisms of polymeric membranes prepared by wet phase inversion</i> . Journal of Applied Polymer Science, 1996. 61 (10): p. 1821-1830.	© 1999 - 2016 John Wiley & Sons, Inc.	28/07/2016	yes	3917750586129
37	figure	Fig. 1. Scanning electron micrographs of cross-sections of membranes ca42st from 15 wt.% PVDF solutions in different solvents.	Bottino, A., et al., <i>The formation of microporous polyvinylidene difluoride membranes by phase separation</i> . Journal of Membrane Science, 1991. 57 (1): p. 1-20.	© 2016 Elsevier B.V.	28/07/2016	yes	3917811222084

38	figure	Figure 1 Isothermal phase diagram for PVDF K-760/water/solvents ternary system at 25°C.	Yeow, M.L., Y.T. Liu, and K. Li, <i>Isothermal phase diagrams and phase-inversion behavior of poly(vinylidene fluoride)/solvents/additives/water systems</i> . Journal of Applied Polymer Science, 2003. 90 (8): p. 2150-2155.	© 1999 - 2016 John Wiley & Sons, Inc.	28/07/2016	yes	3917811416005
42	figure	Figure 8 Scanning electron micrographs of cross-section of PVDF hollow fibers coagulated in ...	Kong, L.F. and K. Li, <i>Preparation of PVDF hollow-fiber membranes via immersion precipitation</i> . Journal of Applied Polymer Science, 2001. 81 (7): p. 1643-1653.	© 1999 - 2016 John Wiley & Sons, Inc.	28/07/2016	yes	3917851323883
47	figure	Fig. 5. Schematic of surface modification of PVDF membrane.	Liu, F., et al., <i>Progress in the production and modification of PVDF membranes</i> . Journal of Membrane Science, 2011. 375 (1-2): p. 1-27.	© 2016 Elsevier B.V.	29/07/2016	yes	3918291370554
55	figure	Fig. 1. SEM images of membrane top surfaces: ... and (D) membrane d- MP-g-P NMP	Chen, C., et al., <i>Forming mechanism study of unique pillar-like and defect-free PVDF ultrafiltration membranes with high flux</i> . Journal of Membrane Science, 2015. 487 : p. 1-11.	© 2016 Elsevier B.V.	29/07/2016	yes	3918300611739
57	figure	Figure 1. a) Formation of a superhydrophilic underwater superoleophobic PAA-g-	Zhang, W.B., et al., <i>Salt-Induced Fabrication of Superhydrophilic and Underwater</i>	© 1999 - 2016 John	29/07/2016	yes	3918300846021

		PVDFmembrane by a salt-induced phase-inversion process. b) Photograph of an as-preparedPAA-g-PVDF membrane ...	<i>Superoleophobic PAA-g-PVDF Membranes for Effective Separation of Oil-in-Water Emulsions.</i> Angewandte Chemie-International Edition, 2014. 53 (3): p. 856-860.	Wiley & Sons, Inc.			
62	figure	Fig. 2. SEM micrographs of the top surface (left), cross-section (middle), and bottom surface (right) morphologies of PVDF membranes by freeze method.	Mu, C.X., et al., <i>Fabrication of microporous membranes by a feasible freeze method.</i> Journal of Membrane Science, 2010. 361 (1-2): p. 15-21.	© 2016 Elsevier B.V.	29/07/2016	yes	3918301094359
64	figure	Fig. 2. SEM images of a cylindrical bulk scaffold ... Fig. 3. SEM image of a bulk scaffold frozen in a planar geometry ...	Madihally, S.V. and H.W.T. Matthew, <i>Porous chitosan scaffolds for tissue engineering.</i> Biomaterials, 1999. 20 (12): p. 1133-1142.	© 2016 Elsevier B.V.	29/07/2016	yes	3918310098178