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High-performance polyvinylidene fluoride
(PVDF) membranes prepared by the Combined
Crystallisation and Diffusion (CCD) method

Submitted by

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Statement of Originality

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Vatsal Shah

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July 2021

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Abstract

This work focuses on making PVDF ultrafiltration (UF) membranes by the new innovative Combined Crystallisation and Diffusion (CCD) method. The combined crystallisation and diffusion (CCD) method is a membrane fabrication technique based on a unidirectional freezing approach to fabricate porous membranes. The CCD method offers much better process control and batch reproducibility compared to the traditional methods used in industry such as the non-solvent induced phase separation (NIPS) and the thermally induced phase separation (TIPS). The CCD membranes have also shown to have much better permeances than their commercial counterparts with similar rejections. This work carried out three main studies, with each focusing on controlling the permeation rate, rejection capability and surface hydrophilicity of the CCD membranes respectively. The innovative dual-layer casting approach applied to CCD membranes in this study allows one to independently control the tightness of the separation layer, and improve the porosity in the support layer, which allows one to further enhance the membrane permeances while still maintaining the separation pore sizes. With this technique, it was for the first time that PVDF membranes with pore sizes of ~ 30 nm had pure water permeances (PWP) as high as ~ 2400 LMH.bar⁻¹, which is almost 15 times higher than traditional NIPS membranes. With regards to influencing the membranes' rejection properties, a simple blending approach using PMMA as the additive was discovered. This is a cost and energy-efficient alternative to reduce the pore size compared to other routes such as increasing the total polymer loading or the cooling duty. Increasing the blender proportion progressively reduced the mean flow pore sizes of the membranes to below 20 nm which is then capable of producing safe drinking water by rejecting most viruses by size exclusion. For improving the membrane surface hydrophilicity, polydopamine (PDA) modification was applied to the CCD UF membranes, and the results showed good permeance recovery post BSA fouling. In fact, the PWP of fouled membranes were still higher by almost 3.5 times than that of fresh (un-fouled) commercial membranes. This showcased the true potential of CCD membranes for real-life applications and its ability to be able to challenge the well-established industry standards.

Keywords: CCD, Crystallisation, PVDF membrane, Ultrafiltration, Fouling

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1 Introduction

1.1 Motivation

One of the most pressing issues of the 21st Century is the sustainable use of water. It is estimated that about 2.1 billion people lack access to safely managed drinking water [1]. According to WHO, water scarcity affects four out of ten people on the planet [2]. With the ever-increasing world population and ineffective water resource utilization, the water demand will keep increasing and the availability of usable water keep decreasing, leading to a scarcity of this vital resource. Due to climate change, many affluent cities around the globe like Cape Town and Chennai are facing record droughts, with “Day Zeros” being imminent in near future. People need to queue in lines to claim their rations of the region’s most precious commodity-clean drinking water [3, 4]. Perhaps that is why it is suggested that water will be the oil of the 21st Century [5]!

Given this challenge of water scarcity that poses the world today, effective water management has become extremely important and the role of membrane technology in dealing with the same shall be significant [6]. Already significant progress has been made in the membrane technology where membranes are used for industrial and domestic wastewater treatment, seawater desalination, provision of potable water among many other applications in other fields ranging from those found in food and beverage to pharmaceutical industries. Today membrane technology has replaced many of the conventional wastewater treatment and distillation separation methods because of its numerous advantages such as lower energy requirements, simpler installations, lower footprint and easier operations and maintenance, leading to a reduction in the total operating costs. In 2019, the membrane separation technology market was estimated at approximately 13.5 billion USD and is expected to grow at a compounded annual growth rate (CAGR) of 6.4% to reach 19.6 billion USD by 2025 [7]. Ultrafiltration (UF) and Microfiltration (MF) technologies contribute to over 50% of the total membrane filtration market because of their wide use in water-based separation applications.

Membranes are produced from a wide range of materials available today. However, among all the types, polyvinylidene fluoride (PVDF) is the most commonly used material for UF and MF applications. This is because of its very desirable properties such as high chemical and thermal resistance, excellent mechanical strength and most importantly its ability to

withstand chlorine disinfection, making it one of the most suitable membrane materials for use in water treatment applications [8, 9].

Despite the numerous advantages, PVDF membranes face several challenges such as low permeation rates and high fouling, owing to the hydrophobic nature of PVDF [8, 10-13]. Typical commercial PVDF membranes have pure water permeance less than 150 LMH bar⁻¹ with pore sizes in the range of 0.02 µm - 0.1 µm (See Table 2.3 in section 2.10.2)[13]. Permeance is defined as the volume of fluid that is filtered through as permeate across a specific membrane area, in a given time and under an applied differential pressure of one bar. Therefore, when using PVDF membranes to process large quantities of feed water, large membrane areas are required to compensate for its low permeance. This leads to a larger footprint requirement, which therefore leads to increased installation and maintenance costs.

The two most commonly used methods of membrane fabrication are the non-solvent induced phase separation (NIPS) and the thermally induced phase separation (TIPS). NIPS has the advantage of producing a tight skin-like separation layer, most suitable for UF applications but has too many controlling parameters that could influence the membrane morphology [8, 10-13]. These might be difficult to control and therefore the membranes suffer from many defects [14]. TIPS, on the other hand, is relatively easier to control, with better batch reproducibility, but fails to generate a tight skin like separation layer on its own [14, 15]. Moreover, both these phase inversion techniques have reached their technological limit, with no significant breakthrough in recent years [13].

So to tackle the problems presented by the conventional fabrication techniques in general and to overcome the technological limit that has reached in performance of the PVDF membranes for ultrafiltration applications in particular, a new fabrication technique of combined crystallisation and diffusion (CCD) was developed [13]. This technique is an adaptation of the “freeze casting” method where the media in which the material is dispersed, is frozen into a network of solid crystals, which serve as pore templates after freeze-drying [16]. CCD involves casting a polymer solution on a solid support and rapid unidirectional cooling is applied much below the freezing point of the solvent. This leads to the formation of solvent crystal nuclei, which then start to grow in the direction of the temperature gradient, owing to the unidirectional cooling applied. The polymer molecules are ejected out of the solvent crystals and eventually solidify surrounding them. The solidified cold membrane is

then placed in an ice-cold water bath to leach the solvent crystals out of the membrane, resulting in the final porous wet membrane ready for use [13].

Preliminary results obtained for PVDF CCD membranes seem extremely promising, with its membranes exhibiting significantly higher permeances without compromising the separation performance, better mechanical properties and higher abrasion resistance [13]. However, this method is still in its nascent stage with many areas yet left to be explored. These unexplored areas present the opportunity to develop this technology and understand it even further to pave way for an alternative manufacturing route to produce PVDF membranes with much superior performance.

1.2 Thesis Objective

Given the potential of this new innovative CCD method and the wide popularity of PVDF membranes for water filtration applications, the overall objective of this thesis is to develop, explore and apply the CCD method to PVDF membranes to tailor its properties such that they can be made suitable for drinking water production. Since most viruses are larger than 20 nm in size, the aim is to be able to produce membranes that can filter out these viruses by size exclusion, also have considerably higher permeation performance than their commercial counterparts [17] and lastly also have anti-fouling properties. The learning outcomes from this thesis will provide the critical technical know-how for large scale CCD based PVDF membrane manufacturing.

After a thorough understanding of the scientific background and extensive literature search and review, the key areas for further research were identified and the objectives to be achieved were set forth. The rationale behind these has been explained later in section 2.14. The specific objectives of this thesis are then set as follows:

- To undertake a systematic study of varying polymer dope solution concentration and observe the effect it has on the permeation characteristics of CCD and NIPS membranes. Additionally, the objective would be to push the upper bound of achievable permeances of the CCD membranes without sacrificing their rejection properties, via a novel way that would involve simultaneous casting of two dopes of different concentrations.

- To reduce the pore size of CCD membranes without modifying the polymer dope concentration or the cooling rate but rather by applying blending modification using poly(methyl methacrylate) (PMMA).
- To modify the surface of CCD membranes using the bio-inspired polymer- polydopamine (PDA), to make it hydrophilic and improve the anti-fouling property of the membranes.

1.3 Thesis Structure

The thesis is divided into 7 chapters as follows:

Chapter 1

This is the introductory chapter (current chapter) which highlights the motivation behind this research project and enlists the thesis objectives.

Chapter 2

This chapter presents the scientific background and literature review section of the thesis. It covers different membrane filtration types and materials and elaborates on the properties of PVDF that sets it apart from other materials. The review then discusses different membrane fabrication methods briefly but then focuses on the two most popular methods used in academia and industry. The recently discovered method of CCD is then introduced and the potential scope of future work is discussed based on which the thesis objectives were finalised.

Chapter 3

This chapter describes the common materials, membrane preparation method and characterisation techniques used in two or more studies, presented in the subsequent chapters of this research project.

Chapter 4 to Chapter 6

A chapter is dedicated to each of the project objectives mentioned above in section 1.2, and so the following chapters (from 4 to 6) present the work done in achieving these.

Chapter 7

The final conclusions drawn from this thesis are summarised in this chapter along with some recommendations for future work.

1.4 References

1. UNICEF, W., *Progress on Drinking Water, Sanitation and Hygiene*. 2017.
2. WHO. *10 Facts on Climate Change*. 2012 [cited 2018 18th May]; Available from: http://www.who.int/features/factfiles/climate_change/facts/en/index5.html.
3. Welch, C. *Why Cape Town Is Running Out of Water, and Who's Next*. 2018 [cited 2018 18th May]; Available from: <https://news.nationalgeographic.com/2018/02/cape-town-running-out-of-water-drought-taps-shutoff-other-cities/>.
4. Karthikeyan, D. *'Our whole life is disrupted': hope dries up as Chennai battles historic drought*. 2019 [cited 2020 04 May]; Available from: <https://www.theguardian.com/world/2019/jun/28/our-whole-life-is-disrupted-hope-dries-up-as-chennai-battles-historic-drought>.
5. Rahaman, M., *Water Wars in 21st Century: Speculation or Reality?* International Journal of Sustainable Society, 2012. **4**: p. 3-10.
6. Tang, C.Y., et al., *Potable Water Reuse through Advanced Membrane Technology*. Environ Sci Technol, 2018. **52**(18): p. 10215-10223.
7. Markets, M.a., *Membrane Filtration Market*. 2019, Markets and Markets: Northbrook, Illinois.
8. Liu, F., et al., *Progress in the production and modification of PVDF membranes*. Journal of Membrane Science, 2011. **375**(1-2): p. 1-27.
9. Ji, J., et al., *Poly(vinylidene fluoride) (PVDF) membranes for fluid separation*. Reactive and Functional Polymers, 2015. **86**: p. 134-153.
10. Guillen, G.R., et al., *Preparation and Characterization of Membranes Formed by Nonsolvent Induced Phase Separation: A Review*. Industrial & Engineering Chemistry Research, 2011. **50**(7): p. 3798-3817.
11. Lee, M., et al., *Formation of micro-channels in ceramic membranes – Spatial structure, simulation, and potential use in water treatment*. Journal of Membrane Science, 2015. **483**: p. 1-14.
12. Hu, N., et al., *Preparation and Characterization of Hydrophilically Modified PVDF Membranes by a Novel Nonsolvent Thermally Induced Phase Separation Method*. Membranes, 2016. **6**(4): p. 47.
13. Wang, B., J. Ji, and K. Li, *Crystal nuclei templated nanostructured membranes prepared by solvent crystallization and polymer migration*. Nat Commun, 2016. **7**: p. 12804.

14. Jung, J.T., et al., *Understanding the non-solvent induced phase separation (NIPS) effect during the fabrication of microporous PVDF membranes via thermally induced phase separation (TIPS)*. Journal of Membrane Science, 2016. **514**: p. 250-263.
15. Wang, B., et al., *Porous membranes prepared by a combined crystallisation and diffusion (CCD) method: Study on formation mechanisms*. Journal of Membrane Science, 2018. **548**: p. 136-148.
16. Scotti, K.L. and D.C. Dunand, *Freeze casting – A review of processing, microstructure and properties via the open data repository, FreezeCasting.net*. Progress in Materials Science, 2018. **94**: p. 243-305.
17. Milo, R. and R. Phillips, *Cell Biology by the Numbers*. 2015: CRC Press.

2 Scientific Background and Literature review

2.1 Introduction

Membranes today have become an important separation technology in chemical engineering and are used in wide-ranging applications. Filtration has been a common household practice for centuries, where one component is easily rejected out while allowing the other to pass through it freely. However, the ability to carry this out at a molecular scale has revolutionised the way separations can be performed.

The first significant application of the membrane-based separation was at the end of World War II when drinking water supplies had broken down around Europe and filters were needed to test for the safety of water [1]. Although membranes were becoming popular, until the 1960s membrane industry was still in its infant stage, with limited application in laboratory setups or small specialised industrial separations [1]. It was after the seminal discovery made by Loeb and Sourirajan to produce defect-free asymmetric reverse osmosis (RO) membranes that had permeation rates 10 times higher than any other membrane available at the time [2-4]. Seawater desalination on a large commercial scale then became a reality and also paved way for the development of ultrafiltration and microfiltration membranes. Today, membrane technology has become exceedingly mature and so many applications such as sterile filtration, hemodialysis, water purification, gas separation and many others are unimaginable without the use of membranes [5, 6].

2.2 Membrane filtration types

Liquid filtration is predominantly a pressure-driven process and depending on the type of application, membranes with specific pore size ranges need to be used. These are categorised into 4 main types listed below:

2.2.1 Microfiltration (MF)

MF membranes have pore sizes in the range of 100-1000 nm. These membranes can filter out large suspended solids such as particulates, colloids, fat and bacteria. However, it allows viruses, proteins, polysaccharides and other relatively smaller molecules to permeate through. They play an important role in primary disinfection and clarification of the uptake water stream from the reservoirs, before entering UF units to produce potable water. Some other important applications include cold sterilization in the pharmaceutical and beverage

industry, separation of casein from whey protein in the dairy industry and production of paints and adhesives [1, 7]. Many times MF membranes are used in pre-treating feed streams to block out larger molecules, before entering UF or RO systems.

2.2.2 Ultrafiltration (UF)

UF membranes have pore sizes in the range of 2-100 nm. Unlike MF membranes, UF membranes are capable of retaining polysaccharides, proteins, viruses and other relatively larger molecules. They, however, allow sugars, amino acids, multivalent and monovalent ions and water to permeate through [1]. UF plays an important role in the production of potable water. Along with MF membranes, UF membranes are also widely used in membrane bioreactors for wastewater treatment and is preferred over the conventional activated sludge systems because of several advantages such as consistent permeate quality, smaller footprint requirement, pathogen-free permeate, and most importantly no chemical disinfection requirement [8]. UF is also widely used in the dairy industry for whey protein concentration, cheese production, and removal of pathogens from milk [9]. UF membranes are also used to pre-treat feed streams entering RO systems, for example in the application of seawater desalination [10]. This project focuses on fabricating UF PVDF membranes.

2.2.3 Nanofiltration (NF)

NF lies in a transition region between pure RO and pure UF with pore sizes in the range of 0.1-1 nm. It is sometimes referred to as loose RO or low-pressure RO [1]. NF membranes are used for the removal of micropollutants and multivalent ions and have partial retention for univalent ions. Their applications include water softening, removal of heavy metals from wastewater, removal of pesticides from groundwater, and wastewater recycling in laundries [11].

2.2.4 Reverse osmosis (RO)

RO membranes have pore sizes that are so small (less than 0.1 nm) that it filters out almost everything such as salts and metallic ions and only allows water to pass through [12]. One of the most important applications of RO membranes is seawater desalination, which is very popular in areas with very limited surface and groundwater [13]. Also, RO membranes are widely used around the globe in household drinking water purification systems to further improve the quality of water. RO systems are also used in industry to ensure that the water heated in the boiler to produce steam to heat various processes, is devoid of salts and minerals, as otherwise would lead to scaling or corrosion [14].

If the UF membrane is composed of parallel cylindrical channels, and assuming that these are all of the same radius, the permeation flux can be described by the Hagen-Poiseuille equation:

$$J = \frac{\varepsilon r^2}{8 \mu \tau} \frac{\Delta P}{\Delta x} \quad \text{Equation 2.1}$$

Here J is the permeation flux, ε is the surface porosity, r is the pore radius, μ is the viscosity, τ is the membrane tortuosity, ΔP is the pressure difference applied and Δx is the membrane thickness.

Equation 2.1 clearly shows that the permeation flux is directly proportional to the driving force obtained as a result of the pressure difference applied and inversely proportional to the membrane thickness and liquid viscosity. If the pores are not perpendicular cylindrical pores, then the membrane tortuosity τ becomes important as it accounts for the additional transport resistance in the path of the flow. It should however, be noted that most ultrafiltration are asymmetric in nature, and so only the top-separation layer mainly determines the transport resistance.

2.4 Membrane Materials

There are over 130 different membrane materials and several new ones are being developed almost every year [16]. However, only a few of these materials are commercially being used today. Materials used for synthetic membrane fabrication can be categorised into two main types- inorganic (or ceramic) and organic (or polymeric).

2.4.1 Inorganic or Ceramic Membranes

Inorganic materials such as aluminium oxide, titanium oxide, zirconium oxide and silicon carbide, are commonly used for making ceramic membranes. When compared to polymeric membranes, ceramic membranes have a better thermal and chemical resistance, ease of cleaning after fouling and inertness to microbiological degradation [17]. However, the fabrication technique requires sintering at high temperatures, which leads to an increase in the cost of production.

2.4.2 Organic or Polymeric Membranes

These are the most commonly used membranes in industry, because of their low cost of fabrication. Among the wide variety of polymeric materials available, the most commonly

used ones for membrane synthesis are cellulose acetate, polysulfone (PSU), polyethersulfone (PES), polyamide and polyimide (PA and PI), polyacrylonitrile (PAN), polyethylene and polypropylene (PE and PP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and polyvinylchloride (PVC) [18].

2.5 Polyvinylidene fluoride (PVDF)

2.5.1 About PVDF

PVDF is the most commonly used material in the fabrication of UF/MF membranes. It is a semi-crystalline polymer with $-(CH_2-CF_2)-$ as the repeating unit. The crystalline phase give PVDF its high mechanical strength, whereas the amorphous phase provides it with good flexibility. PVDF also has good chemical and thermal resistance [19]. PVDF also has a relatively good solubility in organic solvents which makes it easier to make porous membranes from dope solutions. Furthermore, it has good processing ability to be configured into all three membrane geometries i.e. flat sheet, tubular and hollow fibre [20].

2.5.2 PVDF synthesis

PVDF is manufactured commercially by polymerisation of vinylidene fluoride (VDF) $[CH_2=CF_2]$ monomer using a radical initiated process in aqueous suspension or emulsion [21]. In this process, VDF addition is predominated in the “head to tail” orientation, where $-CF_2-$ denotes the “head” and $-CH_2-$ denotes the “tail. However, there may be some defects in the polymer chain because of “head to head” ($CH_2-CF_2-CF_2-CH_2$) or “tail to tail” ($CF_2-CH_2-CH_2-CF_2$) addition that might have taken place instead of the expected “head to tail” ($CH_2-CF_2-CH_2-CF_2$) orientation [22]. These defects are influenced by the process conditions, particularly temperature, and contribute to about 3-6% in the commercial polymers [21]. The crystallinity and other properties of the PVDF are influenced to some extent by these defects.

2.5.3 Crystallinity of PVDF

Impact resistance, toughness and mechanical strength of a polymer are determined by the level of crystallinity. PVDF is a semi-crystalline polymer where the crystallinity can range anywhere between 35 to 70% [21]. The glass transition temperature (T_g) for PVDF is $-40^\circ C$ whereas the melting peaks (T_m) are observed at $156-180^\circ C$ [21].

Four distinct polymorphs of PVDF exist namely alpha (α), beta (β), gamma (γ) and delta (δ) previously called form II, I, III, and IV respectively[21, 23-25]. The most common is

the α -phase where hydrogen and fluorine are placed alternatively on each side to form a TGTG' (trans-gauche) chain conformation. The β -phase PVDF is an all-trans conformation (TT) and the γ -phase PVDF is that between α and β forms with a TTTGTTTG' conformation. The δ -phase PVDF is not very relevant from the practical viewpoint as it is formed under special circumstances by distortion of α -phase form under a high electric field. It is therefore sometimes known as the polar form of α -phase, having the same chain conformation as the α -phase form. Figure 2.2 shows the schematic representation of α , β and γ phases of PVDF [26].

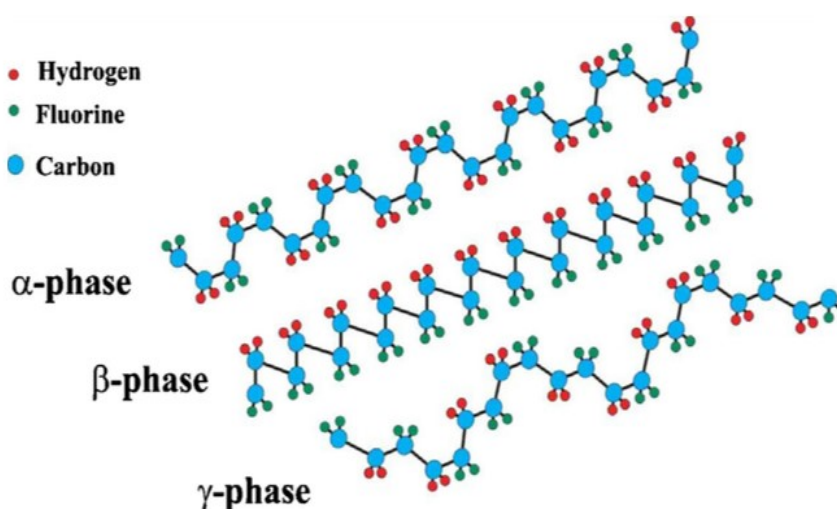


Figure 2.2 Schematic representing the chain conformations for the different phases of PVDF [26]

The crystallisation of the polymer is dependent on various parameters such as thermal history, cooling rates, polymerisation method, molecular weight and molecular weight distribution [27]. Many studies have been published that discuss the role of fabrication conditions on membrane morphology and polymer crystallisation [28-38].

Wang et al. investigated the effect of coagulation bath temperature on the crystallinity of PVDF membranes prepared via NIPS approach, with Dimethylacetamide (DMAc) as the solvent and water as the non-solvent [28]. It was found that at a higher bath temperature of 60°C, the crystallites consisted of only α phase PVDF, while at a lower coagulation bath temperature of 15°C, the total membrane crystallinity increased and crystallites consisted of both α and β phases. Cheng carried out a similar investigation at 25°C and 65°C for 1-octanol/DMF/PVDF and concluded that the lower temperature produces crystals in both phases, with β phase dominating, whereas the higher temperature produces crystals only in the α phase [29].

There are other studies that investigated the effect of polymer dissolution temperature on the morphology and crystallinity of the membranes [30, 31]. Lin et al. studied a 1-octanol/N,N-dimethylformamide(DMF)/PVDF/ system, where PVDF was dissolved in N,N-DMF at different temperatures and then cooled down to 25°C, before immersing in 1-octanol coagulation bath at 50°C [30]. The morphology of the membrane was characterised by an increase in the size of the spherulites as the dissolution temperature increased. Wang et al. also did a similar polymer dissolution temperature study for water/N,N-DMAc/PVDF system, with the coagulation bath temperature at 25°C [31]. This time the membrane morphology was characterised by interconnected cavities, which increased in size as the dissolution temperature increased. In both the studies, the dissolution temperature did not affect the crystal phase as it was α - phase PVDF for all, nor did it change the total crystallinity very much [30, 31].

Another study shows the dependence of crystallinity and mechanical strength on the annealing temperature and the cooling rate [32]. PVDF (with a self-made additive) hollow fibre membranes were made via the NIPS approach, with DMAc as the solvent and water as the non-solvent. The prepared membranes were annealed at increasing temperatures and cooled at varying cooling rates. The total crystallinity, breaking strength and α to β ratio in the outer surface increased with an increase in the annealing temperature, until the point when the temperature was too close to the melting point, when these values declined. A decrease in the cooling rate increased the total crystallinity and the breaking strength but did not affect the α to β ratio in the outer surface of the membrane.

Haponska et al. studied the effect of molecular weight and the coagulation temperature on the crystallinity of the prepared PVDF NIPS membranes with N-methyl-2-pyrrolidone (NMP) as the solvent and water as the non-solvent [33]. As the molecular weight was decreased, the proportion of beta phase to alpha phase in the membrane top surface increased. In line with the results of the studies mentioned above, an increase in the coagulation bath temperature leads to a preferential crystallization in the α phase over the β phase.

Another study investigates the effect of different preparation methods such as NIPS, melt spinning and solution-cast methods on the crystallisation behaviour and tensile strengths of PVDF membranes [34]. The results showed that both the methods NIPS and melt spinning, produced hollow fibre membranes where the skin was composed of both α and β phase PVDF, whereas the overall membrane was predominantly α phase PVDF. NIPS process, however, produced membranes where the total percentage crystallinity was 60% with no spherulites in

the morphology whereas melt spinning membranes had 48.7% crystallinity with perfect spherulites. For the solution cast method, it was slightly more complicated, where the evaporation temperature and the self-made soluble additive determined the crystallinity and the membrane morphology. The study concluded that more than the crystallinity, it was the crystalline morphology that determined the tensile strengths of the membranes, which was found to be much higher for those with perfect spherulites.

For PVDF membranes produced by the TIPS process, mainly the choice of diluent, the cooling rate (determined by the difference between dope temperature and the quenching temperature) and the choice of additives are the factors that determine the polymorphic form and the overall crystallinity of the final membranes [35]. Generally, in a TIPS process, the kinetically favourable α phase PVDF is preferred, however dipole-dipole type interactions induced under certain conditions may also produce β phase PVDF. There have been some studies that suggest the formation of γ phase PVDF either alone or in coexistence with α phase when diluents such as gamma-butyrolactone (γ -BL) and dibutyl phthalate (DBP) have been used respectively [36, 37].

In conclusion, α and β phases are the most common polymorphic forms found in PVDF membranes, with the γ phase being formed under certain special conditions. The role of kinetics in conjunction with the thermodynamics hence determine the final crystalline phase of PVDF obtained [39]. Cui et al. present an excellent review of how various fabrication methods influences the formation of crystalline polymorphs in PVDF membranes [38].

2.5.4 Chemical stability of PVDF

PVDF is known for its chemical stability in various chemical environments such as strong acids, oxidising agents, various solvents (aliphatic, aromatic, and chlorinated), salts and halogens at elevated temperatures [23]. It also has excellent abrasion resistance and resists damage from ultraviolet and nuclear radiation [21]. This chemical inertness makes PVDF a popular choice for making membranes as it can be used for various filtration applications.

It is the presence of fluorine that makes PVDF chemically and thermally resistant. The backbone of a fluorinated polymer is formed by C-C bonds and the pendant groups are C-F bonds. Both these bonds are extremely strong with high dissociation energies. Moreover, high electronegativity and the small size of fluorine atoms keep them close to the backbone and cover it uniformly, thereby protecting it from chemical attack, rendering the polymer

chemically inert and stable [40]. The higher the number of fluorine atoms, the better is the coverage and therefore more inert the polymer is. Therefore, despite PVDF being so stable in various chemical environments, is less inert than PTFE, as PTFE has more fluorine atoms attached to the C-C backbone [41].

PVDF is also unable to withstand environments that are either alkaline or have a presence of amines, esters and ketones. PVDF stability in alkaline environments is of particular concern, because PVDF membranes may be employed for use in wastewater treatment or in membrane contactors for acid gas absorption, where they would be exposed to strong alkaline solutions. There have been several studies that suggest PVDF degradation upon exposure to sodium hydroxide (NaOH) or potassium hydroxide (KOH), as it attacks the α -phase of PVDF, leading to noticeable colour change from the original white to brown to finally black after a few hours of exposure at above ambient temperature [42-47]. The degradation was suggested to be due to the elimination of hydrogen fluoride molecules resulting in the formation of C=C and C $\equiv$ C bonds as was revealed by the FTIR results [42, 45, 48]. These results have been well summarised in a review study that suggests that the chemical attack is further aggravated at increased temperatures and in presence of catalysts [19].

2.5.5 Thermal stability of PVDF

As a semi-crystalline fluorinated polymer, PVDF is known for its good thermal stability too. A study conducted by Furusho et al. compared the thermal stability of several halogen-containing polymers such as PVDF, PVF (polyvinyl fluoride), PVB (polyvinyl bromide), PVdB (polyvinylidene bromide), PVC (polyvinyl chloride), and PVdC-VC (Vinylidene chloride-vinyl chloride copolymer) by evaluating the temperatures at which shear modulus begins to decrease [49]. PVDF (followed by PVF) was the best performing polymer because the bond energy associated with the carbon-halogen bond is the highest for the polymer that contains fluorine atoms.

The glass transition temperature (T_g) for PVDF is -40°C [21]. For the melting point of PVDF, one must look at the three main crystalline phases of PVDF, wherein each one melts at a different temperature. The most thermally stable phase is the γ phase, followed by the α phase, and the least stable is the β phase [50]. β phase PVDF is found to be completely melted away at 170°C , whereas α phase melts away completely at 180°C . The most stable γ phase has a melting point above 190°C .

Given their high thermal resistance, PVDF membranes are therefore usually unaffected when exposed to feeds at elevated temperatures for prolonged durations. One of the studies tested the performance of commercial Kynar PVDF UF spiral wound membrane modules for 7 months for a feed stream that simulated textile sizing wastewater [51]. PVDF showed no signs of degradation in this duration where the temperature of the feed stream was at 85.5°C with an operating pressure at 20-25 psi.

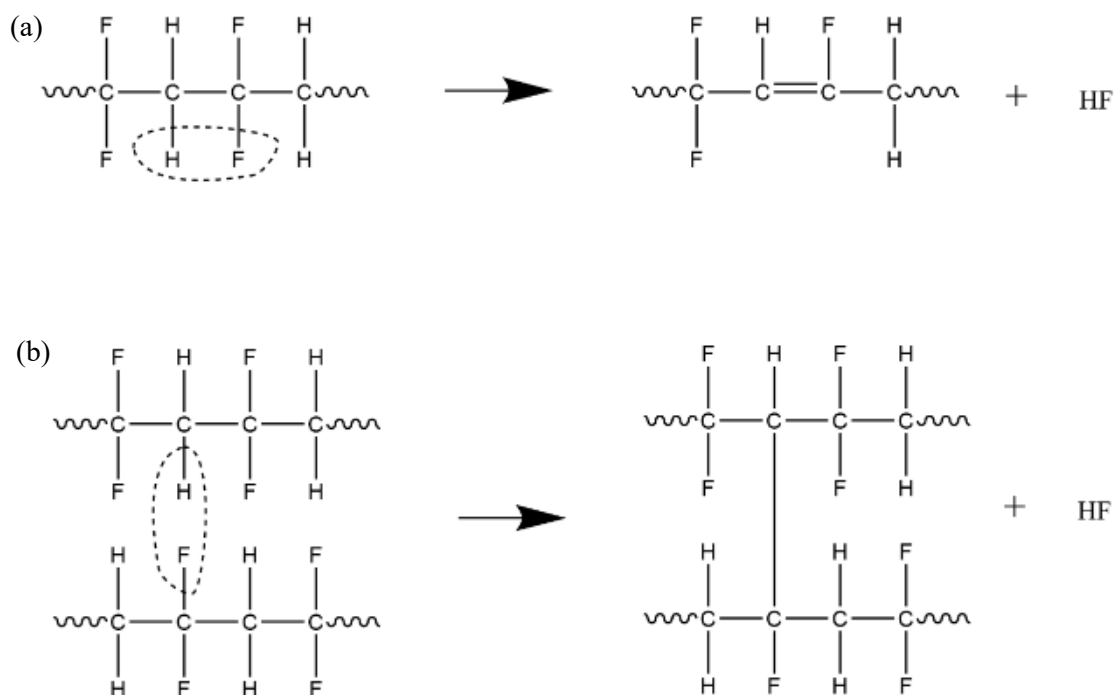


Figure 2.3 Schematic showing the two dehydrofluorination reaction mechanisms in PVDF: (a)Formation of conjugated chain (b)Crosslinking of PVDF (adapted from [19])

PVDF is however susceptible to thermal degradation upon prolonged exposure to high temperatures above 300°C. It could cause chemical reactions to occur which might lead to discolouration of PVDF. The main reaction that occurs at high temperature is the dehydrofluorination reaction where hydrogen fluoride is lost and results in the formation of conjugated $-\text{CH}=\text{CF}-\text{CH}=\text{CF}-$ chain. This is what explains the observed discolouration; however, the rate of degradation is dependent on the percentage of defects in the original PVDF resin. The defects are dependent on the number of “head to head” or “tail to tail” units that might have occurred instead of the expected “head to tail” repeat units during the VDF addition process for PVDF synthesis. Therefore, the higher the number of defects, the higher will be the interruption in the dehydrofluorination reaction, leading to its slower discolouration [19, 21].

The main reaction might also be coupled with a side reaction where cross-linking of PVDF may occur. Figure 2.3 shows the schematic mechanism of the two dehydrofluorination reactions that occur at high temperatures [19].

Above 350°C thermal decomposition of PVDF occurs, leading to the formation of hydrofluoric acid, carbon dioxide and water. In case of incomplete burning, carbon monoxide and low molecular fluorocarbons may also be evolved [52].

2.5.6 Mechanical strength of PVDF

What differentiates PVDF from other fluorinated polymers is its mechanical properties. PVDF has high mechanical and impact strength, as well as outstanding resistance to both, creep under long-term stress and fatigue upon cyclic loading when compared to other perfluorocarbon polymers that are softer and mechanically less robust [21]. In fact, among the fluorinated polymers, PVDF has the best mechanical properties with the highest tensile strength and flexural modulus over a wide temperature range [53, 54]. This tendency to resist deformation makes PVDF membranes so suitable for filtration applications, where the membranes are under stress due to the operating pressure for long durations.

2.5.7 Solubility of PVDF in organic solvents

According to a study by Bottino et al., eight of the 46 liquids that were investigated were found to be good solvents for PVDF [55]. These include N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), hexamethyl phosphoramide (HMPA), trimethyl phosphate (TMP), triethyl phosphate (TEP), tetramethylurea (TMU), dimethyl sulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP). This solubility of PVDF in common organic solvents simplifies the preparation of the dope solution, used for membrane casting.

To conclude this section on PVDF, these properties are what makes PVDF a popular choice for membrane fabrication. The good solubility of PVDF in various organic solvents simplifies the manufacturing process and makes it economical to produce porous membranes on a large scale in industry, while the other properties such as good thermal and chemical resistance and excellent mechanical strengths allow PVDF membranes to show excellent performance during operation for various filtration applications. Today, PVDF accounts for a large share in the UF and MF membrane market. It is widely used in both domestic and industrial wastewater treatment, potable drinking water plants, in pre-treatment units for water desalination [19, 56, 57]. Apart from water-related applications, PVDF membranes are used in

bioethanol recovery, membrane contactor, bio-medical applications, separators for lithium-ion batteries, gas separation units and as supports to make composite membranes [19, 56].

The next section focuses on different fabrication methods for making PVDF membranes.

2.6 Membrane Preparation Methods

PVDF membrane fabrication started in the early 1980s and the membrane preparation methods have progressed and refined since then [58]. There are several methods to make PVDF membranes such as sintering, track etching, phase inversion, and electrospinning. These are summarised below [19].

2.6.1 Sintering

The sintering process involves heating compressed powder material at elevated temperatures just below the melting point, to weld the particles in the powder together to yield one single mass of a porous membrane structure with good mechanical strength. This technique is mainly used in the commercial production of inorganic membranes. It is also employed to make PTFE and PP membranes due to their low solubility in solvents. Sintering is rarely the method of choice for PVDF membranes, but there have been a few patented works that employ the sintering method [59, 60]. One work involves dispersing PVDF powders in methyl isobutyl ketone (MIBK), atomising the dispersion in a spray drier to give dried spherical PVDF particles which are then sintered to produce porous PVDF structures [59]. Another work involved the sintering of a PVDF substrate layer with a PVDF membrane layer [60]. POREX Filtration Group ® has patented this technology and is commercially available as POREX tubular membrane modules.

2.6.2 Track Etching

Track Etching method involves subjecting a polymer film to a normally applied high-energy particle radiation (metal ions) beam. These particles pass through the film resulting in tracks of a certain diameter. The total number of the tracks developed also depend on the exposure time to high-energy radiation. The polymer film with “tracks” are then exposed to an acidic or alkaline bath of etchant solution that “eats” away the polymer starting from its weakest points- the tracks and widens the tracks into full-fledged pores. The diameter of the pores can be controlled by controlling the concentration, temperature and exposure time of the etchant to the irradiated polymer film [61, 62]. The result is the formation of porous membranes with

uniform pore size distribution [19]. Research work has been done on producing PVDF membranes by this method, however, commercial production remains expensive and cannot compete with the more popular phase inversion by immersion precipitation [19, 61].

2.6.3 Electrospinning

In the electrospinning process, a high electric field is applied to a polymer solution or melt passing through a fine needle. The droplet at the tip of the needle is stretched horizontally to form a pendant shape (Taylor cone), as the electrostatic repulsion of the charged liquid molecules counteracts the surface tension forces. Soon enough, a jet of continuous liquid stream erupts from the droplet, the solvent evaporates and fibres formed are simultaneously wound on a support attached to a rotating drum, forming the membrane surface [63]. Figure 2.4 shows the schematic of an electrospinning process [64].

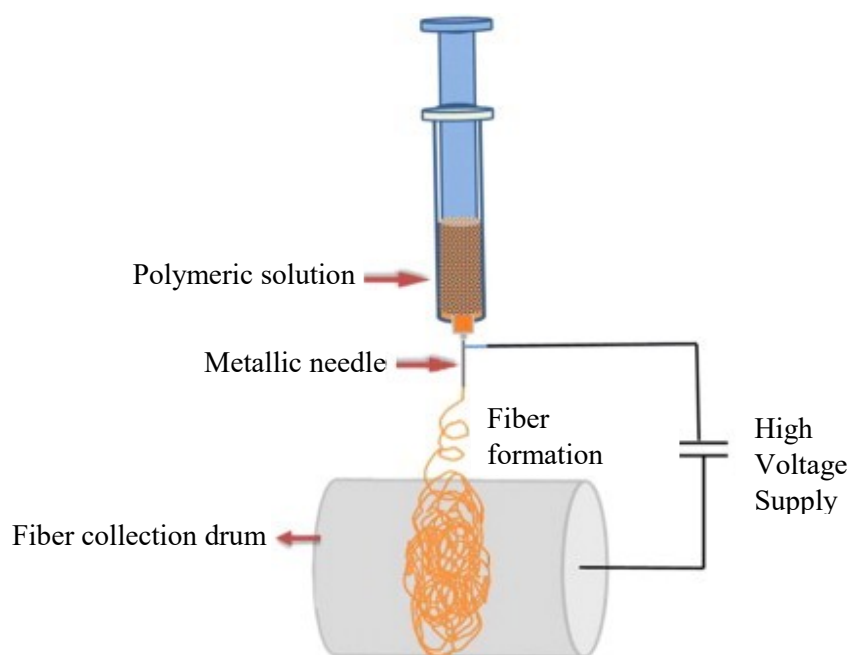


Figure 2.4 Schematic of electrospinning setup [64]

Electrospun nanofibrous membranes have numerous attributes that make it an attractive method, such as high porosity, wide pore size ranges (from nanometres to micrometres), interconnected open pore structure, large surface area per unit volume, high permeance and tailorable membrane thickness [19]. Nonetheless, these membranes require additional support to provide it high enough mechanical strength for practical applications. PVDF electrospun membranes have been produced by many researchers [65-67], however, making large-sized

membranes on a commercial scale remains challenging owing to its limited production capacity and reproducibility [64].

2.6.4 Controlled Stretching

In this method, a semi-crystalline polymer is extruded close to its melting point with a very rapid drawdown. The crystallites arrange themselves in the direction of the drawdown. The extruded film is then annealed to allow for further molecular transition into the crystalline phase. The film is then stretched in the direction perpendicular to the drawdown direction leading to a partial fracture in the film, resulting in a porous membrane [1]. Many times, the stretching step is carried out in two steps- a cold stretch followed by a hot stretch [68]. The membranes produced by the controlled stretching method have very low permeance and are less popular for commercial production. Moreover, this method is more common for PTFE or polyolefins (such as polypropylene (PP)) and has hardly ever been applied to PVDF [69, 70].

2.6.5 Phase Inversion

The phase inversion method remains one of the most common methods for membrane preparation and specifically for PVDF, because of its solubility in common organic solvents as mentioned above in section 2.5.7. PVDF is dissolved in an organic solvent to make the dope solutions, which are then cast into the desired geometry which would either be flat sheet, tubular or hollow fibre. Phase inversion is then elicited by one of the following techniques such as solvent evaporation, precipitation by controlled evaporation, non-solvent induced phase separation (NIPS), thermally induced phase separation (TIPS) or vapour induced phase separation (VIPS). A new method of phase inversion technique that was recently discovered is called combined crystallisation and diffusion (CCD) [71, 72]. Any of the above phase inversion techniques, cause the initially thermodynamically stable homogenous solution to undergo demixing and separate into two phases, one of which is a polymer-rich phase and the other a solvent-rich phase. Following phase inversion, a solvent extraction step is carried out if necessary, to give final solidified porous membranes. Each of the phase inversion techniques is briefly described below [73].

a) Precipitation by solvent evaporation

In this method, a polymer is dissolved in a solvent, cast on a suitable support (such as a glass plate, a nonporous polymer or a non-woven fabric) and placed in an inert environment (such as nitrogen) devoid of moisture. As a result, the solvent evaporates and a homogenous dense membrane is formed [74].

b) Precipitation by controlled evaporation

In this method, the polymer is dissolved in a mixture of more volatile solvent and less volatile non-solvent. After casting the homogenous solution on a suitable support and allowing for the more volatile solvent to evaporate, the composition shifts to a higher non-solvent and polymer content, which leads to phase separation and polymer precipitation. An asymmetric membrane with a skinned top layer is formed [75].

c) Vapour induced phase separation (VIPS)

In this method, a polymer dissolved in a solvent is cast and placed in an atmosphere where the vapour phase consists of a non-solvent saturated with the same solvent in which the polymer is dissolved. The evaporation of solvent from the cast film is therefore negligible because of the high solvent concentration in the atmosphere. Instead, the non-solvent penetrates into the cast film, and when it reaches a high enough concentration, phase separation takes place and a porous membrane without a top layer is obtained [74].

d) Thermally-induced phase separation (TIPS)

TIPS method or thermal precipitation involves dissolving the polymer in a solvent at a suitable elevated temperature to form a uniform dope solution. The solution is cast on a suitable support and cooled down to a temperature where the polymer solution is unstable and starts to demix. Once the phase separation is completed and membrane precipitated, a solvent extraction step is followed to remove any remaining solvent from the polymer matrix [75]. The solvent extraction step is also carried out in the above-mentioned methods, for similar reasons. Typically, the TIPS method produces membranes with isotropic structures [76].

e) Non-solvent induced phase separation (NIPS)

NIPS method or immersion precipitation involves casting a homogenous polymeric solution on a suitable substrate and then immersing the cast film in a coagulation bath containing a non-solvent, which usually is deionised water. Upon immersion, the solvent diffuses out, while the non-solvent diffuses in. This solvent - non-solvent exchange leads to phase separation and the solidified porous membrane is obtained. Typically, asymmetric membranes with skin-like separation layers are obtained [74, 77].

f) Combined crystallisation and diffusion (CCD)

This is a new method of membrane fabrication discovered only recently in 2016 and is still in its nascent stage [71, 72, 78]. It involves a unidirectional cooling approach to cast film

to produce asymmetric membranes with a tight separation layer and microporous sublayer. The phase separation is induced by crystallisation of solvent and subsequent solidification (through gelation and/or crystallisation) of the polymer. The porosity is determined by the oriented growth of the solvent crystallites from the separation layer to the sub-layer.

NIPS process remains one of the most commonly used methods in the industry to make PVDF membranes, owing to the simplicity and flexibility it offers in obtaining the desired membrane morphologies [19, 56]. TIPS method, though less common than NIPS, is known for the ease of control of process parameters, and so is the second most popular method for making PVDF membranes [37, 56, 79-81]. The CCD method, although new, has numerous advantages over the traditional methods and has shown very promising preliminary results for PVDF membranes. These three methods are described in detail below.

2.7 Non-solvent induced phase separation

As described before, a typical NIPS process would involve immersion of a cast film made up of polymer dope solution in a non-solvent medium, which would lead to precipitation of the polymeric membrane upon phase separation due to the solvent – non-solvent exchange.

2.7.1 NIPS Mechanism

To understand the mechanism of NIPS, one must consider the ternary phase diagram because of the three components involved in a typical NIPS process- the polymer, the solvent and the non-solvent. The three corners of the ternary phase diagram represent these three components in their pure forms. Any point lying on the sides of the triangle represent a binary mixture of the corresponding corner components forming that side, while any point inside the triangle represents a ternary mixture. The important features of a ternary phase diagram include the binodal, spinodal, and tie lines and the critical point. Figure 2.5 shows the schematic of a ternary phase diagram of a polymer-solvent-nonsolvent system [82]. When the cast film composed mainly of the polymer dissolved in the solvent (with dilute amounts of or without any non-solvent), it lies in a thermodynamically stable single homogenous phase region. When this film is immersed in a non-solvent, the system could undergo four different composition paths labelled 1-4, and each could result in four different structures represented by the corresponding rectangles shown just underneath the phase diagram (the polymer-rich phase is represented by the hatched areas in the rectangles) in Figure 2.5.

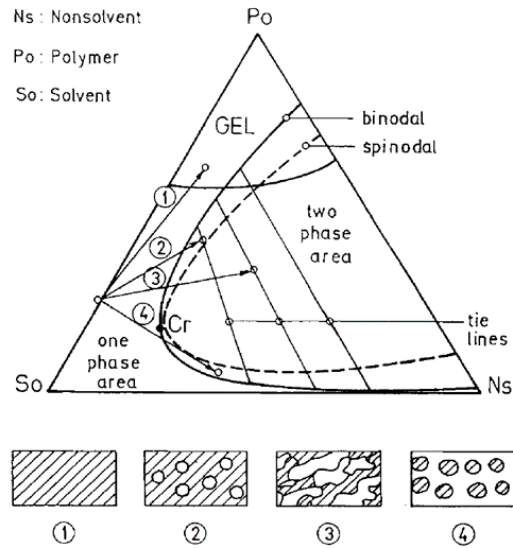


Figure 2.5 Ternary phase diagram of a polymer-solvent-nonsolvent system showing different composition paths that can take place during a NIPS process [82]

The composition path 1 enters the “gel” region, which represents the polymer solidification region, where the polymer could undergo either gelation and/or crystallisation and/or glass transition. This path occurs when the rate of outflow of the solvent is much higher than the rate of inflow of the non-solvent. Factor “K” is defined as the ratio of solvent diffusion out of the cast film to non-solvent diffusion into the cast film. Therefore, here $K \gg 1$. The resultant membranes are compact, dense and impermeable in UF conditions.

The composition path 2, where again the solvent diffusion out is faster than non-solvent diffusion in ($K > 1$), enters the metastable region above the critical point. If there are large enough composition fluctuations, to enable the formation of nuclei, phase separation will take place by nucleation and growth of polymer-lean phase in polymer-rich phase, resulting in a membrane with non-interconnected dispersed pores.

The composition path 3 enters the unstable region delimited by the spinodal boundaries. This path is followed when $K < 1$. Spinodal liquid-liquid demixing occurs and both the phases grow and interconnect to form a three-dimensional bicontinuous network. Since PVDF is a semi-crystalline polymer, solid-liquid demixing may also occur.

The composition path 4 ($K \ll 1$) also enters the metastable region but this time below the critical point. Again, if there are high enough fluctuations in the concentration, nucleation and growth of the polymer-rich phase in the polymer-lean phase occurs. When the

concentration of nuclei and the speed of its growth are high enough, the beads stick together to form a compact polymeric membrane, else low integrity powdery agglomerates are formed.

For the composition paths 2-4 described above, after phase separation takes place, the polymer-rich phase solidifies as the solvent diffuses out and moves up closer towards the gelation line. PVDF membrane is a semi-crystalline polymer, so solidification of the membrane takes place by both crystallisation and gelation.

2.7.2 Influencing factors for NIPS

In practice, the formation of the membrane via NIPS is a complicated process. Various parameters may affect the morphology and performance of PVDF membranes formed via the NIPS process[19]. These are summarised below.

2.7.2.1 Choice of solvents

The choice of solvent is a very important parameter that controls the morphology of the PVDF membranes. Bottino et al. in their earlier study had found that out of the 46 liquids they had investigated, eight of them, which includes DMAc, DMF, DMSO, HMPA, NMP, TEP, TMP and TMU, were good solvents for PVDF [55]. They studied the effect of these solvents on the PVDF membrane morphology and concluded that the morphology of PVDF membranes (indirectly characterised by permeance and porosity measurements) depended not on the thermodynamic properties but rather on the kinetics governed by the mutual diffusivities of the solvent-non-solvent [83]. The non-solvent used was water. Figure 2.6 shows the SEM of the PVDF membrane cross-sections prepared using different solvents [83].

Another study [84] also investigated the morphologies for PVDF membranes using different solvents and water as the non-solvent. The solvents considered were DMAc, DMF, NMP and TEP and the cross-sectional morphologies of the prepared membranes were in line with ones obtained by Bottino et al. [83], with TEP producing membranes having uniform sponge-like symmetric structure. The reason for this was attributed to the relatively weak solvent power of TEP compared to other solvents, because of which a small amount of non-solvent would induce liquid-liquid phase separation and therefore the membrane would precipitate at an early stage. Moreover, the relatively weak mutual affinity of TEP and water compared to other investigated solvents results in the sponge-like morphology.

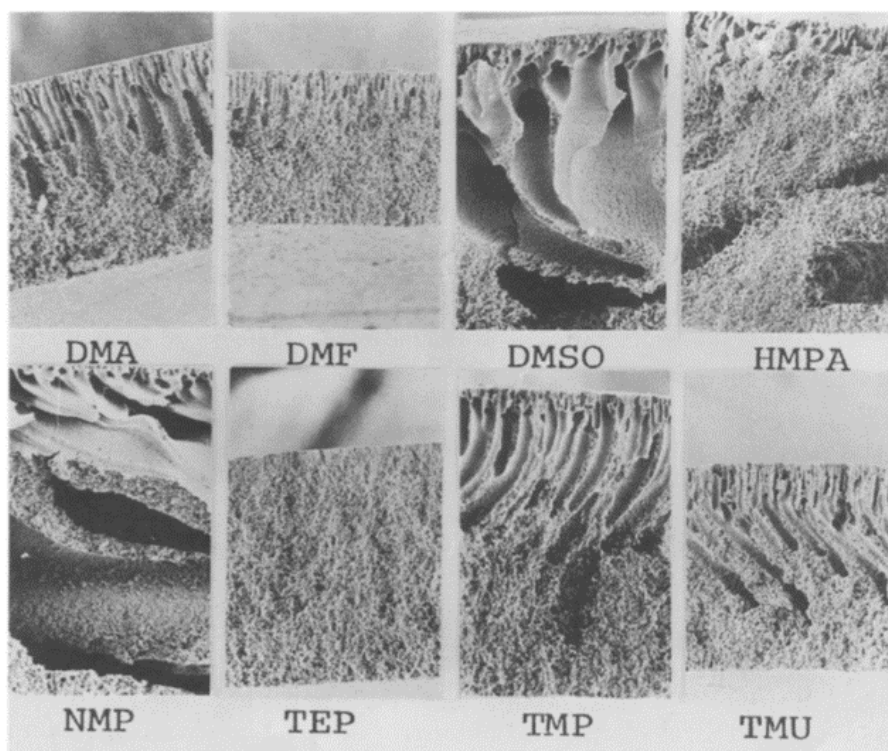


Figure 2.6 Scanning electron micrographs of cross-sections of PVDF membranes prepared using different solvents [83]

Li et al. studied the effect of solvent power on the NIPS membrane morphologies in greater detail by considering four different mixed solvents [85]. TMP-DMAc and TEP-DMAc represented solvent mixtures with high solvent power while tricresyl phosphate (TCP)-DMAc and tri-n-butyl phosphate (TBP)-DMAc represented ones with low solvent power. The high solvent power mixtures resulted in faster precipitation of membranes characterised with finger-like voids, less membrane shrinkage and higher permeance.

2.7.2.2 Evaporation time

Evaporation time can also be a factor affecting the morphology of the prepared PVDF membranes. Once the dope solution is prepared and cast on a suitable support, and before immersing it in the coagulation bath, the cast film could be left out for some solvent evaporation to take place. This would influence the membrane morphology as now after solvent evaporation, the top layer would have a higher polymer concentration than the rest of the cast film, which would therefore influence the solvent-nonsolvent diffusion rate. This was particularly evident when dope solutions were prepared with high boiling point solvents (DMF or NMP) mixed with low boiling point solvents (acetone or THF) [86].

2.7.2.3 Use of non-solvent additives in the dope solution

The membrane morphology can also be tailored to the desired structure by the addition of non-solvent additives in the dope solution. The function of an additive could be to either act as a pore-forming agent, accelerate the phase separation process or increase the viscosity of the dope solution. These additives could be categorised into two main types:

- Non – polymeric or low molecular weight additives

One of the widely investigated non-polymeric additives is Lithium Chloride (LiCl) [87-91]. As per literature, it was found flat sheet membranes prepared with a higher LiCl concentration in the dope solution, lead to an increase in the size of the cavities resulting in an increased maximum pore size and membrane porosity but a reduction in the mechanical strength of the membranes [90, 91].

Like LiCl, Lithium perchlorate (LiClO₄), another low molecular weight inorganic salt is also investigated in many studies as a non-solvent additive in the dope solution to increase the mean flow pore size of the prepared membranes [84, 92]. The concentration of LiClO₄ and the resultant viscosity of the prepared dopes are again important in determining the morphology of the membranes [92]. Glycerol, 1,2-ethanediol and water are other non-solvent additives that have also been investigated to enhance the demixing process and increase the mean flow pore size of the membranes [93-95].

- Polymeric or high molecular weight additives

PVP is one of the most common and widely studied additives in this category, to produce highly porous membranes. PVP is hydrophilic in nature and therefore its presence in the cast solution promotes the influx of non-solvent water when the cast film is immersed into it and favours the formation of large finger-like voids in both hollow fibre and flat sheet membranes [87, 88, 96, 97]. The molecular weight (MW) of the PVP used is also important, as a low MW PVP is found to create small pores as it easy leaches out of the membrane resulting in high water permeance, whereas high MW PVP remains in the voids and results in path blockages resulting in a considerable reduction in the permeance [96]. PEG is another water-soluble polymer that is reported to improve the permeance [98].

There are many other additives used to improve the surface properties of PVDF, however, these are not covered here, as the focus is on factors that influence the membrane morphology [19, 56].

2.7.2.4 Choice of coagulation bath

Coagulation bath also plays an important role in determining the morphology of PVDF membranes. Its choice will determine whether PVDF will undergo liquid-liquid demixing or crystallisation. For flat sheet membranes, it has been found that the use of water as the coagulation medium, a common practised choice, results in instantaneous liquid-liquid demixing to produce asymmetric membranes with finger-like voids. However, a coagulation medium with added solvent delays the demixing process and results in membranes having sponge-like morphology [99].

1-octanol is a softer non-solvent that is used when crystallisation dominated precipitation is desired. The cross-section structure of flat sheet membranes of a 1-octanol/DMF/PVDF system was found to be symmetric with uniformly packed spherical particles. Contrary to this, a water/DMF/PVDF system produced an asymmetric membrane with finger-like morphology [100].

The addition of ethanol to the water coagulation bath has also been found to change the morphology from a typical finger-like void structure to a sponge-like structure [96]. A study investigated the change in morphology when water is replaced with water/alcohol (50/50) as the non-solvent in a PVDF/NMP/non-solvent system [101]. The alcohols considered were ethanol, methanol and isopropyl alcohol (IPA) and the morphology changed from typical finger-like to a macrovoid-free globule-type structure. The result was attributed to both kinetic and thermodynamic factors that delay the liquid-liquid demixing process and facilitate the crystallisation of the polymer (solid-liquid demixing). Thermodynamic stability of the PVDF/NMP/non-solvent systems follows the sequence: water < methanol < ethanol < IPA as can be seen in the phase diagram shown in Figure 2.7 [101]. From the kinetics viewpoint too, the diffusion coefficients of the non-solvents with respect to the solvent (NMP) correlated with the demixing process and follows the order: water > methanol > ethanol > IPA. The size of the globules formed in the membrane prepared by the alcohol non-solvents follow the order methanol < ethanol < IPA, suggesting a longer delay in liquid-liquid demixing resulting in a longer crystallisation time for the polymer in that order.

In addition to the composition of the coagulation bath, the temperature of the bath would also play an important role in determining the morphology of the membranes. It has been observed that an increase in the coagulation bath temperature leads to the formation of finger-like structures, while a lower temperature leads to the formation of sponge-like or

particulate structures [102]. The lower temperature could lead to either delayed liquid-liquid demixing or crystallisation of the polymer resulting in the formation of the respective structures [29, 84, 102].

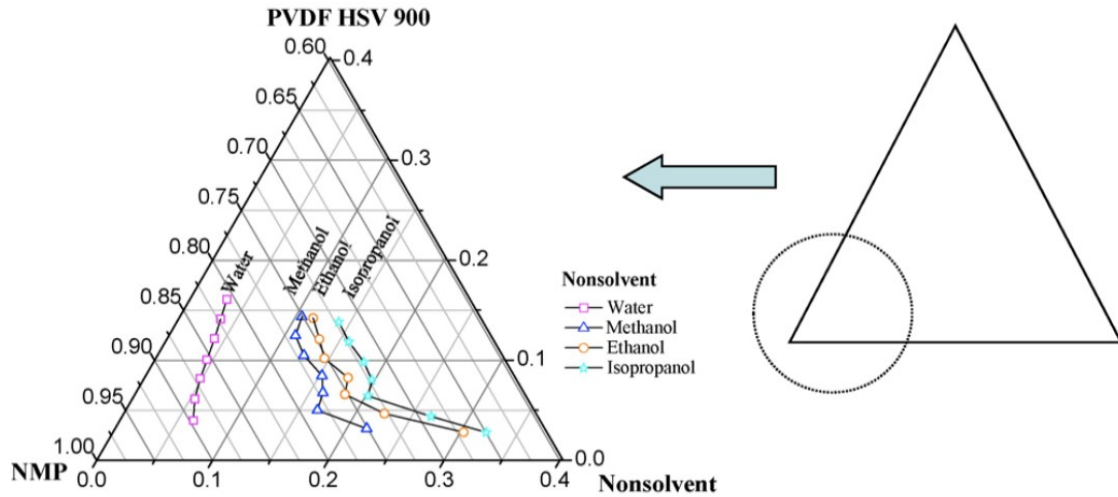


Figure 2.7 Ternary phase diagram of NMP/PVDF/non-solvent systems at 25°C [101]

Although, it may seem that having so many influencing factors may be advantageous as it provides multiple ways to control the membrane morphology, however a good control on all of these together is always challenging. For example, slight variations in the temperature of the casted dope or coagulation bath can influence interdiffusion of the solvent-nonsolvent, or slight changes in humidity can affect the rheology of the dope, or slight delays in immersion can cause evaporation of a solvent. It may be difficult to control all of these simultaneously for every bath. For hollow fibre spinning, it is even more complicated as in addition to the factors mentioned above, other factors such as the height of air gap, extrusion rate and spinneret type can also influence the final morphology. These have been well summarised in the review study done by Liu et al. [19]. Thus, good batch reproducibility is always a challenge for NIPS membranes.

2.8 Thermally Induced Phase Separation (TIPS)

In a typical TIPS process, the polymer is dissolved in a high boiling point solvent with low molecular weight to make a homogenous solution which is then cooled down to a point below the phase boundary to induce phase separation.

2.8.1 TIPS mechanism

To understand the mechanism of TIPS, one must consider a binary phase diagram as opposed to a ternary phase diagram involved in a NIPS process. The polymer composition forms the x-axis while the temperature forms the y-axis. Figure 2.8 represents the schematic of a binary phase diagram that governs a TIPS process for a semi-crystalline polymer [103].

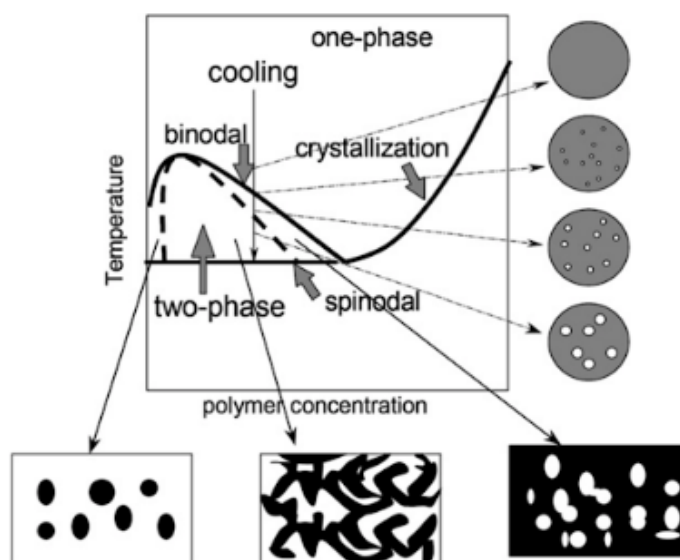


Figure 2.8. Binary phase diagram for a semi-crystalline polymer undergoing TIPS [103]

In the binary phase diagram, a binodal and spinodal curve exist, just as they did in the ternary phase diagram. The region between the two curves is the metastable region. When the cast film composed of thermodynamically stable single homogenous phase solution is cooled down into a phase separation region, the system could undergo four possible composition paths. During cooling, if the composition path ends in the metastable region, liquid-liquid demixing is delayed. This could either be when the composition path enters the metastable region to the left or the right of the critical point. If the fluctuations in the composition are large enough, then phase separation will take place by nucleation and growth of polymer-rich (or lean) phase in polymer-lean (or rich) phase if the metastable region lying to the left (or right) of the critical

point is under consideration resulting in the formation of powdery agglomerates (or membranes with non-interconnected dispersed pores).

If the composition path enters a region inside the spinodal curve, the solution is unstable and liquid-liquid separation occurs. The two phases grow and interconnect to form a bicontinuous network leading to the formation of porous membranes. Whenever the composition path would enter the unstable region, it would pass through the metastable region, however, the effect of this transition is negligible if the cooling rate is fast enough. Once the phase separation is completed upon cooling, a solvent extraction step is carried out to give solidified porous membranes.

Since PVDF is a semi-crystalline polymer, phase separation may also occur by solid-liquid demixing. It occurs when the composition path enters the region below the crystallisation curve as shown in Figure 2.8.

During solid-liquid demixing, the solid phase is formed by crystallisation of pure PVDF, while the liquid phase is a polymer lean solution. The crystallisation of PVDF will occur upon cooling, either when the homogenous solution is high in polymer concentration or the cooling temperature is below the temperature at which the binodal and the crystallisation curve intersect.

2.8.2 Influencing factors for TIPS

Since TIPS involves only two components and is a simpler process compared to NIPS, it has comparatively fewer influencing factors that affecting the membrane morphology. Some of them are listed below:

2.8.2.1 Choice of diluent

The choice of diluent is one of the important factors, that determines whether the cast film undergoes solid-liquid (S-L) demixing or liquid-liquid (L-L) demixing followed by subsequent crystallisation. A strong diluent is one, which has strong interactions with the polymer. A strong diluent favours S-L demixing whereas a weak diluent favours L-L demixing. Li et al. studied this by observing the effect of increasing dioctyl phthalate (DOP) concentrations in dibutyl phthalate(DBP)/DOP mixtures that were used as diluents to prepare PVDF dopes [36]. The results showed that for pure DBP (good diluent), solid-liquid demixing was favoured which resulted in a spherulitic membrane morphology. Contrary to this, diluent mixtures containing relatively higher concentrations of DOP (poor diluent), gave the

membranes a bicontinuous interconnected morphology, which was a result of the liquid-liquid demixing route. Another such study investigated the effect of four different diluent mixtures on the final morphology of PVDF membranes [80]. As the degree of interactions of PVDF–diluent became weaker, the spherulitic structure became less discernible. Many such studies have been focused on finding the correlation between the diluent and the resultant PVDF membrane morphology [36, 37, 79, 80, 104-106].

2.8.2.2 Cooling rate and quenching temperature

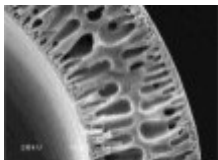
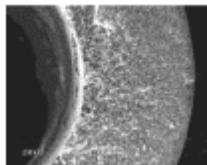
During the solid-liquid demixing process, where phase separation takes place by nucleation and growth of PVDF crystallites, the cooling rate and the quenching temperature are crucial factors in determining the extent of crystal growth. Generally, when the quenching temperature is low, smaller spherulites are obtained. This is because a lower quenching temperature will have a faster rate of cooling, a smaller size of initial crystal nuclei, a faster crystallisation process and so a shorter time duration before phase separation is completed leading to the formation of smaller spherulites [80, 104, 107, 108].

In addition to these basic factors that influence the TIPS process, other factors such as polymer concentration, dissolving temperature, blending dope solutions with polymeric and inorganic additives, and non-solvent concentration are also studied [19].

2.9 Comparison of NIPS and TIPS

Table 2.1 shows the comparison of non-solvent induced phase separation (NIPS) and thermally induced phase separation (TIPS) [56]. NIPS is the most popular method of membrane fabrication for UF applications because of its ability to form asymmetric membranes with tight skin that forms the separation layer. However, there are several influencing factors as discussed above that need to be controlled effectively to give the membranes the desired structure. Controlling so many factors independently is always difficult and hence makes batch reproducibility very challenging. Comparatively, TIPS has fewer influencing factors, which makes process control and batch reproducibility relatively easier [81]. TIPS membranes also have fewer defects than NIPS membranes. However, TIPS alone cannot give a tight separation layer with small pore sizes and therefore make it a less popular method for UF applications.

Table 2.1 Comparison of NIPS & TIPS methods for PVDF membrane preparation [56].

Item	NIPS method	TIPS method
Solvents or diluents used	DMAc, DMF, NMP, THF, DMSO etc.	Triacetin, sulfolane, dimethyl phthalate (DMP), dibutyl phthalate (DBP) etc.
Influencing parameters for membrane fabrication	More	Less
Processing temperature	Lower	Higher
Minimum pore size of membrane	Smaller	Larger
Pore size distribution	Wider	Narrower
Typical microstructure of PVDF membrane prepared		
Mechanical strength of membrane	Weaker	Stronger
Antifouling property	Better	Lower
Major disadvantage	Recovery of solvent	High energy consumption

There have been some works that modified the usual TIPS process to produce asymmetric or anisotropic membranes. Evaporation of diluent before phase separation or by imposing a temperature gradient across the membrane during the quenching process have shown to be effective methods. Caneba and Soong developed anisotropic poly(methyl methacrylate) (PMMA) membranes through the modified TIPS approach [109]. They designed a special cell, where the cast film was sandwiched between a Teflon plate (insulator) and a metal plate, and tightened with bolts to prevent any leakage. The single homogenous cast film was then cooled from the thermally conducting metal side, by running room temperature water over the metal. The side that was cooled preferentially had smaller pores compared to the opposite side, and lead to the formation of an anisotropic membrane. Similarly, Tsai and

Torkelson also employed the same procedure to make PMMA anisotropic membranes [110]. Matsuyama et al. developed polypropylene anisotropic membranes by carrying out evaporation for a set duration to create a polymer concentration gradient in the cast film and then followed it with the general cooling procedure involved in TIPS [111-113]. Similarly, Caplan et al. in their study explained the formation of skins in a TIPS process and attributed it to two factors [114]. First, cooling the membrane by surface contact lead to a faster cooling rate at the surface than in the interior, which resulted in faster crystallisation and solidification of the skin layer compared to the interior. Second, the evaporation of the diluent from the surface lead to a concentration gradient being formed which resulted in the formation of a separation layer that was denser than the interior.

The above-mentioned works that modified the TIPS method to produce anisotropic or asymmetric membranes complicate the simple TIPS process and make process control again very difficult. Moreover, the skins produced by these membranes are few microns thick, which make them not very suitable for high-throughput applications [71, 109-113].

There have also been efforts where NIPS and TIPS have been combined, where a high-temperature homogenous cast film is quenched in a cold non-solvent bath [81, 115-118]. This method is known as the non-solvent thermally induced phase separation (NTIPS) method. NTIPS is however even more complicated than sole NIPS and TIPS process.

2.10 Compilation of permeation characteristics for PVDF-UF membranes

2.10.1 Lab-made UF PVDF membranes

Various literature studies on UF PVDF membranes were referred to, to generate a comprehensive list that provides the permeation characteristics (pure water permeance (PWP), mean pore sizes (MPS) and the pore size distribution (PSD)) of these membranes. Table 2.2 presents this list. Most of these membranes are prepared by the NIPS method, as TIPS is usually the less preferred method for making UF membranes.

Table 2.2. Compilation of mean pore sizes (MPSs), pore size distribution (PSD) range and pure water permeances (PWP) of UF PVDF membranes from various literature works*

Modification	Membrane	MPS (nm)	PSD (nm)	PWP (LMH.bar⁻¹)	Ref.
Pure PVDF membranes	PVDF with varying solvents	UF		69	[83]
	PVDF with mixed solvents	40 ± 2		143	[119]
	PVDF with increased evaporation time (airgap)	69		152	[96]
	PVDF with ethanol as internal coagulant	88		155	[96]
Modified with small molecular additives	PVDF with small molecular additives	45		291	[120]
	PVDF with ethylene glycol as non-solvent additive	34	12-70	25	[121]
	PVDF with 1,2 ethanediol as non-solvent additive	36	12-75	49	[122]
Modified with polymeric additives	PVDF blend with PVP	44		309	[123]
	PVDF blend with PVA	47		259	[123]
	PVDF blend with PMMA	20	8-50	209	[124]
	PVDF blend with cellulose nanocrystals	31		207	[125]
Modified with inorganic additives	PVDF blend with LiCl.H ₂ O and TiO ₂	34		82.5	[126]
	PVDF blend with TiO ₂ nanoparticles	47		112	[127]
	PVDF blend with Al ₂ O ₃ nanoparticles		20-50	200-225	[128]
	PVDF blend with SiO ₂ sol	99	Max 540	301	[129]
	PVDF blend with TiO ₂ nanowire	44		266	[130]
	PVDF blend with graphene oxide	55		458	[131]

Modification	Membrane	MPS (nm)	PSD (nm)	PWP (LMH.bar ⁻¹)	Ref.
	PVDF blend with graphene oxide and PVP	UF		360	[132]
	PVDF blend with reduced graphene oxide and TiO ₂ nanocomposites	76 ± 2		77	[133]
	PVDF blend with graphene oxide	12.6 ± 0.1		27	[134]
Modified with inorganic additives (continued)	PVDF blend with zinc oxide-graphene oxide composites	43 ± 2		171	[135]
	PVDF blend with graphene oxide and TiO ₂	65		488	[136]
	PVDF blend with Zinc-Iron oxides nanoparticles	29		224	[137]
	PVDF blend with graphene oxide-PEG nanocomposites	25 ± 1		94	[138]
	PVDF blend with TiO ₂ -HNTs nanocomposites	94 ± 1		354	[139]
	PVDF blend with hydrothermal carbon nanospheres	58		950	[140]
	PVDF blend with Mg-Al nanolayered double hydroxide	55	25-85	351	[141]
	PVDF blend with PVP and graphene oxide nanoribbons	62		532	[142]
	PVDF blend with PVP-TiO ₂ -dopamine	64		243	[143]
	PVDF blend with nano-ZnO particles	31		147	[144]
	PVDF blend with TiO ₂ -activated carbon	31 ± 7		225	[145]

Modification	Membrane	MPS (nm)	PSD (nm)	PWP (LMH.bar ⁻¹)	Ref.
	PVDF blend with Fe ₃ O ₄ -palygorskite nanocomposites	21 ± 1	18-24	356	[146]
	PVDF blend with Mg-Al LDH nanoparticles	32		107	[147]
	Hydroxyl functionalized PVDF-TiO ₂	60	20-120	50	[148]
	PVDDF blend with grapheneoxide-TiO ₂ nanocomposites	78 ± 2		75	[149]
	PVDF with modified with polydopamine polymerisation and ammonium fluotitanate hydrolysis	UF		228	[150]
Modified with graft/block copolymers	PVDF blend with PFSA-g-graphene oxide	77		587	[151]
	PVDF blend with sulfonated poly(α,β,β -trifluorostyrene)	40-50	10-70	103	[152]
	PVDF blend with poly(aminoanthraquinone)/reduced graphene oxide	11 ± 1		70	[153]
	PVDF modified with self-doped sulfonated polyaniline	UF		160	[154]
	PVDF blend with PMMA-b-PSBMA	30	20-40	188	[155]
	PVDF blend with PVP-g-MMT nanocomposites	16		75	[156]
	PVDF blend with SiO ₂ -g-PDMS nanoparticles	16		115	[157]
	PVDF blend with PVDF-g-PMEMA	58		77	[158]

Modification	Membrane	MPS (nm)	PSD (nm)	PWP (LMH.bar ⁻¹)	Ref.
	PVDF-blend with PVDF-g-PEGMA	73	Max 390	777	[159]
	PVDF-blend with PVDF-g-PEGMA	31	Max 183	5170	[160]
Other methods	PVDF with graphene oxide-water as coagulation bath	91		460	[161]
	Electrospun PVDF nanofibers with top chitosan layer	UF		205	[162]

*Many studies characterise pore sizes in many different ways and do not follow a standardised method. Therefore, these values should be used for reference purposes only to get an approximate idea of the membrane's separation capabilities. Also the reporting of pure water permeances varies significantly across various studies. For some studies the pure water flux (L.m⁻².hr⁻¹ or LMH) values were read off from the figures and so would only be approximate values. These values have been converted using the operating conditions mentioned in the respective studies to units of permeances which is LMH.bar⁻¹ (L.m⁻².hr⁻¹.bar⁻¹) to allow for fair comparison. Moreover, this table is not an exhaustive list of all PVDF membrane related studies. Many studies work on PVDF microfiltration membranes and these have not been included in this table. Many studies that do focus on PVDF-UF membranes, either do not characterise the pore sizes or have gas permeance data instead of water permeance. Again these studies are not covered here.

As can be seen from Table 2.2 that for pure PVDF UF membranes, the pure water permeance is only around 150 LMH.bar⁻¹. Many researchers have tried various modification strategies to improve the permeance of PVDF UF membranes [19, 56]. These include either using different solvents or solvent mixtures [83, 84, 119], trying different additives [84, 126, 163-166], or even changing coagulation bath conditions [96, 161, 167] as was elaborated above in section 2.7.2. These do increase the permeation performance of the membrane but do so only marginally or at the cost of the membrane's separation capabilities. Using graft copolymer (such as PVDF-g-PEGMA) in the dope solution can sometimes be very effective at improving the pure water permeances of PVDF-NIPS membranes [159, 160, 168, 169]. But the mechanical strengths of the membrane deteriorate significantly because of the formation of the undesirably large macrovoids in its cross-section [169-171]. Its pore size distribution is also wide with pore sizes ranging from 20-160nm [160]. This makes its application for commercial use rather challenging.

2.10.2 Industry-made PVDF UF membranes

Most UF PVDF membranes in industry are also prepared via the NIPS method. Table 2.3 presents the permeation characteristics of PVDF membranes produced by various industrial manufacturers.

Table 2.3. Pore sizes and Pure water permeances (PWP) of UF PVDF membranes produced commercially by industry leaders^a

Supplier	Membrane Brand	Pore size (nm)	Operating conditions from data sheets ^{b,c,d}	PWP ^e (LMH.bar ⁻¹)	Ref.
Dow-Dupont	IntegraPac	30	Filtrate Flux = 40-90 L.m ⁻² .hr ⁻¹ Max TMP = 2.1 bar	40-90	[172]
	IntegraFlux	30	Filtrate Flux = 40-110 L.m ⁻² .hr ⁻¹ Max TMP = 2.1 bar	40-110	[173]
Suez	ZeeWeed 1000	20	Flow range = 55-110 m ³ .day ⁻¹ Membrane area = 41.8-51.1 m ² TMP range = 0-0.9 bar	61-122	[174]
	ZeeWeed 1500	20	Flow range = 45-180 m ³ .day ⁻¹ Membrane area = 55.7 m ² TMP range = 0-2.76 bar	34-135	[175]
Hydranautics	HYDRAcap MAX	80	Filtrate Flux = 34-110 L.m ⁻² .hr ⁻¹ Max TMP = 2 bar	34-110	[176]
KOCH	PURON	30	Production range = 2-6.8 m ³ .hr ⁻¹ Membrane area = 51 m ² Max TMP = 1.7 bar	40-133	[177]
QUA	EnviQ	40	Filtrate Flux = 10-25 L.m ⁻² .hr ⁻¹ TMP range = 2 psi-4 psi	72-180	[178]
TORAY	MEMBRAY	80	Design Flow = 8-53 m ³ .day ⁻¹ Membrane area = 70 m ² TMP = 0.2 bar	24-158	[179]

^aThe pure water permeances and pore sizes were obtained from specification data sheets published by the supplier. These data sheets were obtained from their respective websites.

^bDifferent data sheets present filtration specifications in different ways. For some data sheets use the terms such as “Flow range”, “Production range” or “Design flow” instead of “Filtration flux” or “Permeation flux”. This value is assumed to be the permeate flow range and not the feed flow range in our calculation. This is because if it were to be the feed flow range, the permeate flow would be even lower.

^cA conservative estimate of the transmembrane pressure is taken to maximise the value computed for the Flux. For many products, the operating pressure was not mentioned, but instead the Max TMP (transmembrane pressure) was mentioned. In these cases if the Max TMP was above 1 bar, then for the permeance calculation, the operating pressure was taken as 1 bar and not the Max TMP. This gives a higher value for the permeance.

^dFor Zeeweed 1000, the data sheets provides an approximate range of the membrane area. In this case again, a lower value of the membrane area is taken for the calculation of permeance.

$$\begin{aligned}\text{PWP (LMH.bar}^{-1}\text{)} &= \text{Filtration rate [L/hr}^{-1}\text{]} / (\text{Membrane area [m}^2\text{]} \times \text{TMP [bar]}) \\ &= \text{Filtrate Flux [L.m}^{-2}\text{.hr}^{-1}\text{]}/\text{TMP [bar]}\end{aligned}$$

As can be seen in Table 2.3, that even for industry-standard UF PVDF membranes, where one can presume the preparation conditions would be optimised to get the best performance, the pure water permeance remains rather low around 150 LMH.bar⁻¹ [72, 78]. To meet the operational needs of a filtration process, a larger membrane area is then required to compensate for this low permeance. This in turn limits the applicability of these PVDF filtration units in parts of the globe that are in dire need of effective and economical water treatment systems.

Thus, in addition to the challenges that different fabrication methods present, the permeation performance of these PVDF membranes produced via the traditional routes have reached a plateau. Hence, there is a need for a new fabrication method that is simple yet effective at producing asymmetric membranes with tight separation layers that not only ensure good rejections but also provide high permeance.

2.11 Combined crystallisation and diffusion (CCD)

The CCD method combines the advantages of both the NIPS and TIPS processes. It can generate a tight separation layer just like NIPS as would be favoured for UF applications, and the process control is relatively much simpler like the TIPS process which allows for good batch reproducibility and quality consistency.

2.11.1 Membrane fabrication using CCD method

The CCD method involves casting a dope solution as a flat sheet on a casting plate and then placing the casting plate on a low temperature precooled plate (maintained at -30°C) to induce rapidly cool and freeze the cast film unidirectionally. The solvent used is DMSO as it has a high melting point around 19°C , and therefore provides a large driving force for solvent crystallisation [180]. It is also a greener alternative to the other organic solvents typically used for membrane fabrication. Due to the unidirectional cooling that is applied, the solvent starts to nucleate at the cold end, and then grow in the direction of the temperature gradient towards the warm end. As the crystals grow, the polymer molecules are expelled out and solidify around the crystals. Once the membrane is frozen into a solid, the solvent molecules are leached out by a solvent extraction step in ice-cold water. Ice-cold water is necessary to eliminate any possibility of solvent crystals to melt and re-dissolve the solidified polymer or change the pore structure. Similar to “freeze-drying or ice templating” methods, the solvent crystals, here too, serve as pore and channel forming templates. As the solvent molecules are leached out, the membrane becomes porous. The rapid unidirectional cooling is what is responsible for the unique asymmetric structure characterised by a tight thin separation layer supported by a porous sub-layer [71]. Figure 2.9 below illustrates the casting, cooling, and leaching processes involved in the CCD method.

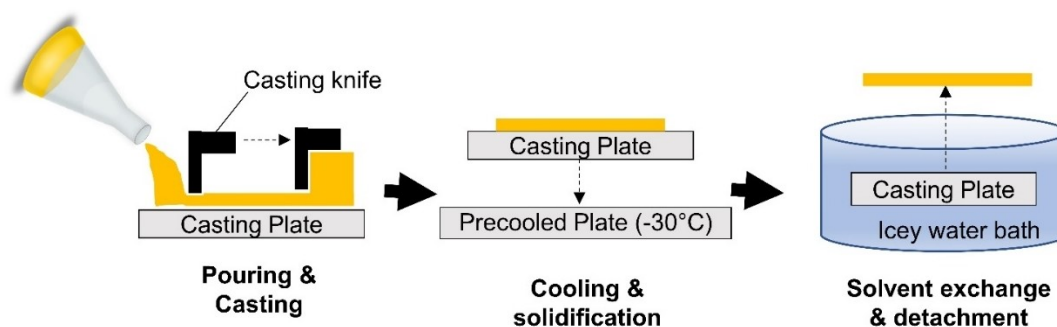


Figure 2.9 Illustration showing the CCD membrane preparation procedure.

2.11.2 Adaptation of Liquid-Solid (L-S) TIPS

This technique is an adaptation of L-S TIPS (and not S-L TIPS), where solvent crystals are also formed by cooling the cast film below the freezing point of the solvent. Generally, in L-S TIPS, the cast film is quenched in a cooling medium (such as liquid nitrogen or precooled hexane) as opposed to unidirectional cooling involved in CCD. The L-S TIPS membranes are shown to produce very large pores around $1\text{--}5\text{ }\mu\text{m}$ which limits its application [72, 181–183].

On the contrary, the CCD method is found to generate asymmetric membranes with pore sizes as low as 30 nm which lies in the UF range [72]. Larger pore sizes can also be achieved via CCD by slowing down the cooling rate through the plates, by either increasing the thickness of the plate or changing the plate type (use glass plates instead of aluminium) [72]. The mechanism for membrane formation via the CCD method is based on the binary phase diagram, as it was for TIPS.

2.11.3 CCD Mechanism

Wang et al. studies the membrane formation mechanism for the CCD technique for PES membrane [71]. The binary phase diagram for PES-DMSO system proposed in that study is shown in Figure 2.10.

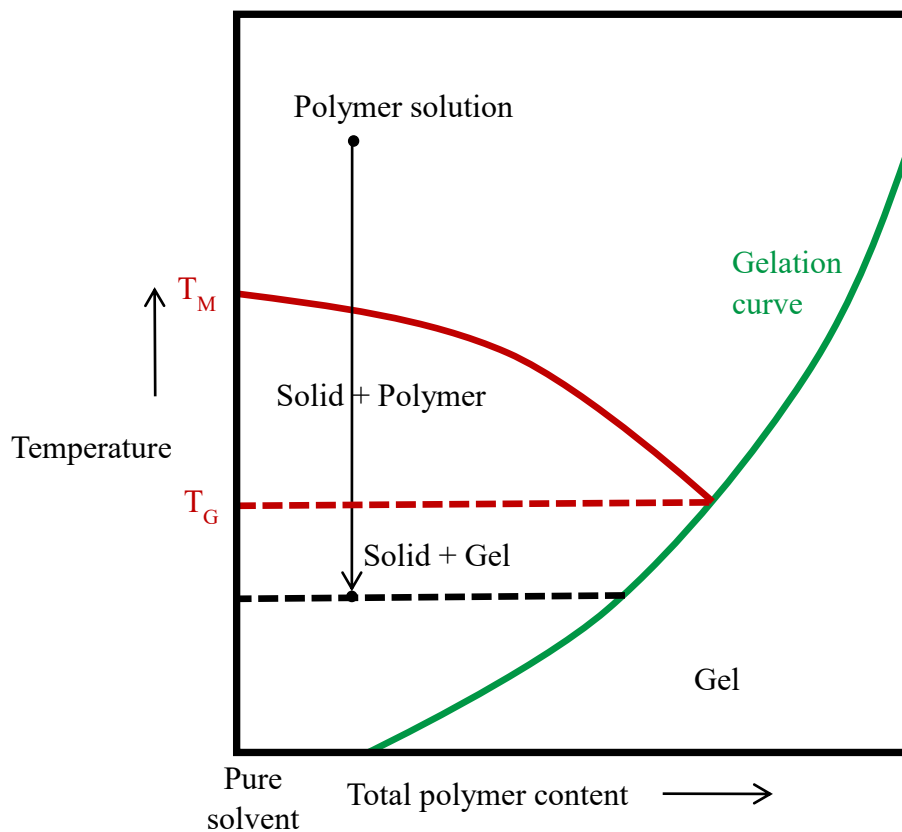


Figure 2.10 Binary phase diagram proposed for CCD (adapted from [71])

Since PES is an amorphous polymer, the crystallisation curve seen in the typical eutectic system is replaced with a gelation curve. The curve on the left-hand side is the solvent crystallisation curve. The gel concentration changes with temperature and therefore it extends beneath the area of solvent crystallisation. When the cast film composed of polymer solution

in its homogenous state is cooled below the melting temperature of the solution (T_m is the melting temperature of pure solvent), solid-liquid phase separation takes place, where solid phase is composed of pure solvent crystals and liquid phase composed of polymer-solvent mixture. As the solvent molecules continue to crystallise out of the solution, the polymer concentration of the liquid phase keeps increasing until it meets the melting curve or the gelation curve depending on what the cooling temperature is. If the cooling temperature is between T_m and T_G (the temperature at which the solvent crystallisation curve meets the gelation curve), the final concentration would be determined by the melting curve, but if it is below the T_G it would be determined by the gelation curve.

PVDF is a semi-crystalline polymer, and therefore it should be noted that phase separation may be interfered by crystallisation of the polymer too. However, since the membrane solidification process is a very rapid process (< 5 s) and crystallisation is a time-dependent process, the general principles behind the mechanism explained for PES should apply to PVDF too. It should be noted that the term gelation is used broadly here to represent the polymer solidification process, on account of increased polymer concentration, characterised by infinitely high viscosity of the solution. It also encompasses other polymer solidification processes that may be accompanied parallelly such as vitrification (for an amorphous polymer such as PES) or polymer crystallisation (for a semi-crystalline polymer such as PVDF) [184-187].

The mechanism of solvent crystal growth involved in CCD, as explained by Wang et al. [71], is summarised briefly here as it will be the basis of future results and discussion sections presented later in the thesis. When the heat is removed through the aluminium casting plate, the temperature of the region in the cast film right adjacent to the casting plate drops down very rapidly, whereas away from the plate, since polymer solution is a poor conductor of heat, the temperature is relatively higher. Therefore, the cast film cross-section can be divided into two regions, a region with a steep temperature gradient that is nearer to the casting plate and another region with a flat temperature gradient away from the casting plate. It must be noted that temperature gradient profile as shown in Figure 2.11 [71], is dynamic and it changes with time, however, this division of region remains roughly valid within the time of interest by which the solidification of the cast film is complete. Different steps involved in the CCD membrane formation mechanism are illustrated in Figure 2.11 [71].

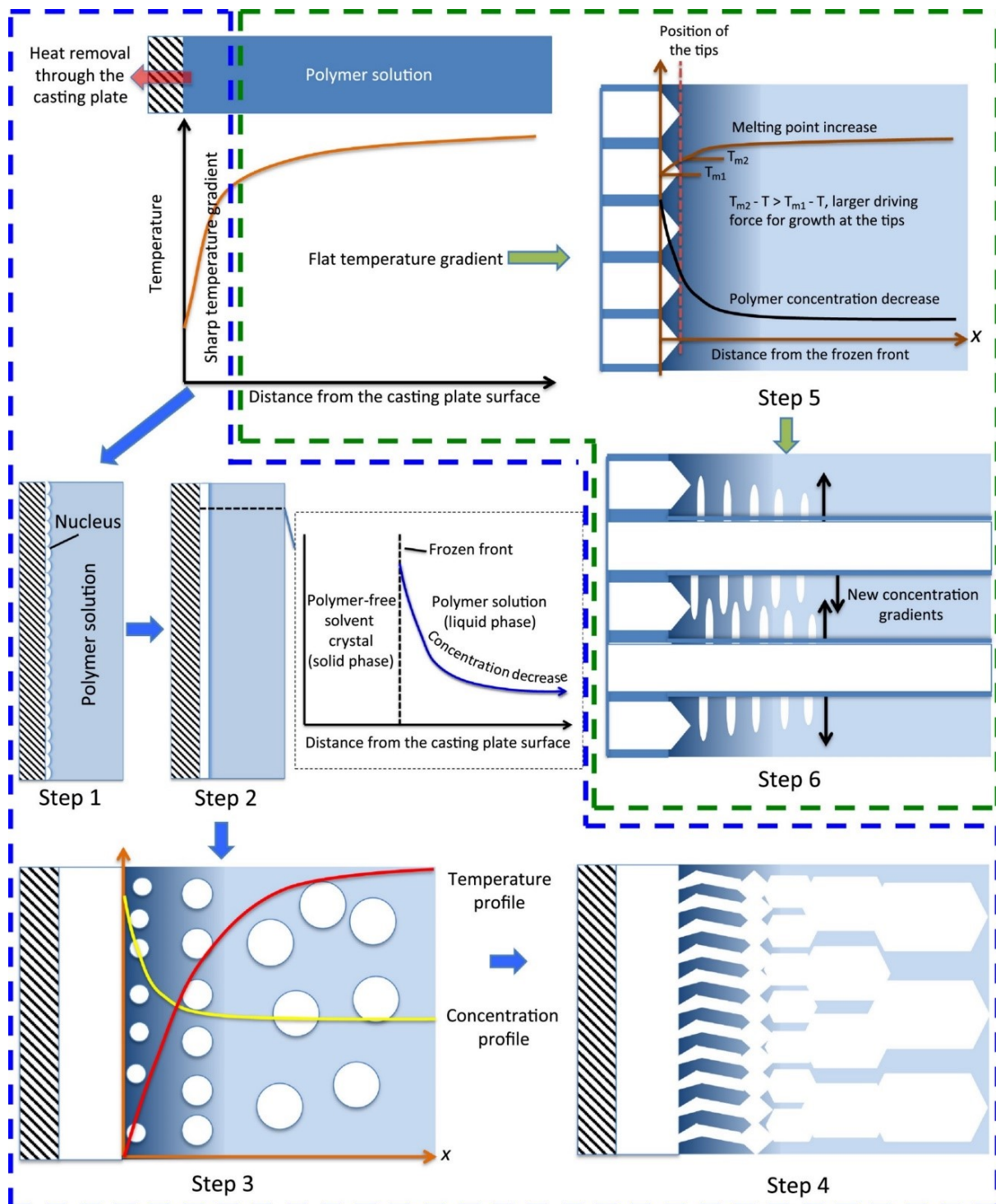


Figure 2.11 Proposed membrane formation mechanism of the CCD method [71] . Steps 1–4 illustrate the formation mechanism of the separation layer in region of steep temperature gradient. Steps 5 & 6 illustrate the formation mechanism of columnar and dendritic structures with a flat temperature gradient. The white parts in the illustration represent the solvent nuclei or crystals.

In the sharp temperature gradient region, nucleation of solvent takes place by heterogeneous nucleation on the surface of the casting plate over homogenous nucleation. This is because the surface provides sites for nucleation and lowers the energy barrier. Very soon, an entire polymer-free solvent frozen front is formed (steps 1 and 2). As the solvent molecules crystallise, it ejects the polymer out from the crystal and therefore a polymer-rich region is formed right next to the frozen front, inducing a polymer concentration gradient. The region adjacent to the frozen front is also very low in temperature, and therefore homogenous nucleation will take place where the size of the nuclei will increase away from the frozen front (step 3). These crystallites will grow larger with time and interconnect and finally lead to an anisotropic pore size distribution in this region of the steep temperature gradient (step 4). The high polymer concentration near this colder end of the membrane cross-section contributes to the formation of a thin but dense separation layer and the small-sized crystals give way to small pores in the separation layer of the final membrane.

In the flat temperature gradient, the temperature is still not low enough, to allow for nucleation to take place, therefore the crystals that developed in the steep or transient temperature gradient region, continue to grow into the flat temperature gradient region. In this region, often columnar (step 5) and dendritic growth (step 6) of the solvent crystal is observed. After solvent extraction, these columnar and dendritic patterns of crystal growth results in interconnected micro-channels in the sub-layer. The final result is an asymmetric membrane with a tight skin separation layer (formed in the steep temperature gradient region) supported by a porous sub-layer (formed in the flat temperature gradient region).

The size of solvent crystals is dependent on the counter diffusion of polymer and solvent molecules at the interface of the solvent crystals. The polymer molecules are diffused out of the growing crystal while solvent molecules diffuse in. This counter diffusion will continue until the polymer concentration adjacent to the solvent crystals reaches the gelation point or the concentration gradients between the solvent crystals become too small. It is because of this **combined** effect of solvent **crystallisation** and polymer-solvent **diffusion** that ultimately produces the characteristic membrane structure, this method is called as the **Combined Crystallisation and Diffusion (CCD)** method.

2.12 Summary of work done in CCD

The CCD method is a relatively new fabrication technique developed in 2016 in the research group led by Prof. Li [71, 72, 188].

In its first-ever study on CCD, various characteristics of CCD membranes produced from PVDF-DMSO dope solution were investigated and compared to their NIPS counterparts [72]. Firstly, the effect of cooling rate on the pore sizes and pure water permeances of CCD membranes was studied. The polymer dope concentration was maintained at 20wt.% while the casting thickness was varied from 0.1 mm to 1mm. Different combinations of casting and cooling plates (Glass-Glass, Aluminium-Glass and Aluminium-Aluminium) were used to vary the cooling rate. The results clearly showed that faster cooling rates produced membranes with smaller pore sizes and lower pure water permeances. Comparing these to the permeation characteristics of NIPS membranes, the CCD membranes have significantly higher permeation rates while still maintaining the pore sizes. Changing the casting thickness of CCD membranes from 1mm to 0.5mm reduced the pore size and the pure water permeance, but a further reduction in casting thickness (0.3 and 0.1 mm) did not change the permeation characteristics very much, but in fact, produced membranes with larger deviations in its pore sizes. All of these results are summarised in Table 2.4 [72].

The mechanical properties of PVDF based CCD membranes were much superior to its NIPS counterpart, given the characteristic interconnected structure and high crystallinity of PVDF in the CCD membranes. Also, CCD membranes were composed mainly of β and γ phases of PVDF as opposed to the large presence of α phase in the NIPS membranes. An accelerated abrasion test was also performed which showed that CCD membranes were capable of still retaining their pore structure, while the NIPS membranes were severely damaged. The BSA fouling test indicated that pure PVDF CCD membranes have a better fouling resistance than the NIPS membranes. Despite its superior performance, there was still a considerable decline in permeance, owing to the hydrophobic nature of PVDF. Blending modification using PEG was applied, however, it may not have really improved the fouling resistance of PVDF membranes as PEG is water-soluble and can easily get washed away during water separation applications. The marginal increase in pore sizes and permeances of PVDF-PEG blend membranes could have been the result of the PEG molecules being leached out and serving as pore formers.

The CC method was also applied to make PES membranes to understand the underlying mechanism behind this method as was explained above in section 2.11.3 [71]. The effect of cooling rate on pore size and pure water permeance was again investigated for PES as was previously done for PVDF [71] and the result was also similar that faster cooling rates produce

membranes with smaller pore sizes and lower pure water permeances. The dope concentration was also varied in this study to see its effect on the pore size. A change in polymer concentration from 15wt.% to 20wt.% while keeping all other parameters constant (such as the cooling rate and casting thickness) changed the pore size from 28 to 23 nm while the pure water permeance reduced from 2286 LMH.bar⁻¹ to 125 LMH.bar⁻¹. Table 2.5 summarises the results of CCD membranes produced from PES-DMSO system [71].

Table 2.4 Summary of permeation characteristics of 20wt.% PVDF based CCD membranes and its comparison with their NIPS counterparts [72].

Membrane Type	Casting/cooling plate combination	Casting thickness (mm)	Pure water permeance (LMH bar⁻¹)	Mean flow pore size (nm)
CCD	Glass/Glass	1.0	10,998 ± 407	345 ± 26
CCD	Aluminium/Glass	1.0	5,017 ± 547	119 ± 10
CCD	Aluminium/Aluminium	1.0	861 ± 78	45 ± 3
CCD	Aluminium/Aluminium	0.5	570 ± 37	29 ± 3
CCD	Aluminium/Aluminium	0.3	608 ± 82	30 ± 9
CCD	Aluminium/Aluminium	0.1	486 ± 28	38 ± 11
NIPS	N/A	1.0	6.9 ± 3.4	35 ± 7
NIPS	N/A	0.5	6.1 ± 1.2	45 ± 9

Table 2.5 Summary of permeation characteristics of PES based CCD membranes studied by Wang et al. [71].

PES dope concentration (wt.%)	Casting/Cooling plate combination	Pure water permeance (LMH.bar⁻¹)	Mean flow pore size (nm)
15	Glass/Glass	11,930 ± 199	664 ± 67
15	Aluminium/Glass	6328 ± 300	121 ± 17
15	Aluminium/Aluminium	2286 ± 29	28 ± 1
15	Stainless steel/Aluminium	1278 ± 198	19 ± 0.6
20	Aluminium/Aluminium	125 ± 51	23 ± 3

2.13 Influencing factors for CCD

Based on the work done on CCD in literature, the two main influencing factors that have been investigated are summarised below:

2.13.1 Cooling rate

It has been observed that if the cooling rate is fast, the mean flow pore size of the membranes is also smaller [72]. This is because a fast cooling rate reduces the temperature of the polymer solution near the plate more rapidly, and therefore the critical nuclei size for the nucleation to occur is even smaller. Also according to the phase diagram, lower temperatures would mean that the polymer solution would reach the gelation point sooner which limits the total time for crystal growth. Additionally, from a kinetic standpoint, the lower the temperatures, the slower would be the solvent-polymer diffusion rates in and out of the growing crystal, which would, in turn, cause the local polymer concentration near the solvent crystal interface to rapidly increase and meet the gelation point sooner, thereby limiting the ability of the crystal to grow larger in size. As a consequence of both these factors, the solvent crystal sizes would be smaller, and a tighter separation layer would be produced [71, 72].

2.13.2 Polymer dope concentration

When different dope concentrations were used (20wt.% and 15wt.%) for making PES membranes, the higher dope solution produced membranes with lower porosities (evidenced by SEM), smaller mean flow pore sizes and lower pure water permeances [71].

These few controlling factors are what makes process control relatively easier in CCD.

2.14 Taking CCD further

Since this method has only been recently invented, and so there are a lot of areas that could be explored such as extending it to other polymers, changing cooling temperatures (as opposed to varying cooling rates) and using different modification techniques. However, the main motivation for this project is to provide alternative high-performance membranes that could reduce the operating and capital costs for water purification systems. This would in turn make the overall purification process economically more viable, paving way for its wide adoption to solve the global water shortage problems. In view of this vision, the research focuses on PVDF as the choice of material for making membranes, given its wide popularity for water-based applications. The CCD technology will be progressively developed further

through the course of this project, to enable effective tailoring of the properties of the prepared membranes as desired.

Membranes are produced in various geometries such as flat sheet, hollow fibre and tubular forms, however, CCD has so far been limited to producing only flat sheets. CCD technique involves unidirectional cooling from a solid substrate, which is inherently challenging to do so for hollow fibres and tubular membranes, given the continuous nature of the spinning process involved. Although developmental work is underway to make CCD universal to all three geometries, the focus of this thesis is limited to flat sheets only.

So far, PVDF membranes were produced only using 20wt.% dope concentration. Wang et al. in their study did vary the dope concentration from 20wt.% to 15wt.%, however, it was done so for PES membranes only. Therefore, a systematic study of varying the dope solution concentration and observing the effect on PVDF CCD membranes has not yet been undertaken and therefore shall be explored further. The permeation performance of these CCD membranes shall be compared to their NIPS counterparts. The hypothesis proposed by Wang et al. in its study explained the formation of the asymmetric structure in CCD membranes and suggested that the separation and support layer can be influenced by not just the cooling rate but also polymer dope solution concentration [71]. Based on this hypothesis, a proof-of-concept study shall be undertaken to influence the separation and support layers individually to push the upper bound of achievable permeances even further while still retaining the separation pore sizes.

Following this, a blending modification using PMMA as an additive shall be implemented, to influence the thermodynamic and kinetic factors, to reduce the pore size of the prepared membranes below 20 nm. This reduction in pore sizes would be brought about by neither increasing the total polymer dope concentration or nor changing the cooling conditions. Membranes with such small pore sizes will be capable of rejecting most viruses, and therefore will make them suitable for drinking water treatment applications.

Despite good rejection and superior permeation characteristics, the adoption of CCD based membranes for water treatment applications would not be possible without improving its anti-fouling property by surface functionalisation. The recently popular method of surface functionalisation using polydopamine (PDA) based coatings shall be applied to CCD membranes and the effect of its deposition time be studied.

The summarised list of thesis objectives that were presented earlier in section 1.2 are also presented here again for the benefit of the reader:

- To undertake a systematic study of varying polymer dope solution concentration and observe the effect it has on the permeation characteristics of CCD and NIPS membranes. Additionally, the objective would be to push the upper bound of achievable **permeances** of the CCD membranes without sacrificing their rejection properties, via a novel way that would involve simultaneous casting of two dopes of different concentrations
- To reduce the **pore size** of CCD membranes without modifying the polymer dope concentration or the cooling rate but rather by applying blending modification using poly(methyl methacrylate) (PMMA).
- To modify the surface of CCD membranes using the bio-inspired polymer- polydopamine (PDA), to make it hydrophilic and improve the **anti-fouling** property of the membranes.

From chapter 4 onwards, every chapter that is presented in the thesis is dedicated to an objective listed above.

2.15 References

1. Baker, R.W., *Membrane Technology and Applications*. 2012, Chichester, UK: Chichester, UK: John Wiley & Sons, Ltd.
2. Loeb, S., *The Loeb-Sourirajan Membrane: How It Came About*, in *Synthetic Membranes*:. 1981, AMERICAN CHEMICAL SOCIETY. p. 1-9.
3. Loeb, S. and S. Sourirajan, *Sea Water Demineralization by Means of an Osmotic Membrane*, in *Saline Water Conversion—II*. 1963, AMERICAN CHEMICAL SOCIETY. p. 117-132.
4. Sidney, L. and S. Srinivasa, *High flow porous membranes for separating water from saline solutions*. 1964, Google Patents.
5. Apel, P.Y., et al., *Prospects of Membrane Science Development*. Membranes and Membrane Technologies, 2019. **1**(2): p. 45-63.
6. Nunes, S.P., et al., *Thinking the future of membranes: Perspectives for advanced and new membrane materials and manufacturing processes*. Journal of Membrane Science, 2020. **598**: p. 117761.

7. SynderFiltration. *What are microfiltration membranes*. 2018 [cited 2018 25 May, 2018]; Available from: <http://synderfiltration.com/microfiltration/membranes/>.
8. Marrot, B., et al., *Industrial wastewater treatment in a membrane bioreactor: A review*. Environmental Progress, 2004. **23**(1): p. 59-68.
9. Tamime, A.Y., *Membrane Processing: Dairy and Beverage Applications*. 2012: United Kingdom: Wiley-Blackwell.
10. Lau, W.J., et al., *Ultrafiltration as a pretreatment for seawater desalination: A review*. Membrane Water Treatment, 2014. **5**(1): p. 15-29.
11. Lenntech. *Nano Filtration and Reverse Osmosis*. 2018 [cited 2018 25th May]; Available from: <https://www.lenntech.com/nanofiltration-and-rosmosis.htm>.
12. Envionment, T.M.R. *Membrane Classifications*. 2018 [cited 2018 25th May]; Available from: http://membranes.edu.au/wiki/index.php/Pore_Size#Microfiltration_.28MF.29.
13. Lee, K.P., T.C. Arnot, and D. Mattia, *A review of reverse osmosis membrane materials for desalination—Development to date and future potential*. Journal of Membrane Science, 2011. **370**(1): p. 1-22.
14. Shah, V., *Emerging Environmental Technologies*. 2008: Springer Netherlands.
15. Radcliff, R.Z., A., *Application of Membrane Technology to the Production of Drinking Water*. Water Conditioning & Purification, 2004: p. 23-25.
16. Cheryan, M., *Ultrafiltration and Microfiltration Handbook*. 1998: Taylor & Francis.
17. SynderFiltration. *Membrane Materials: Organic V. Inorganic*. 2018; Available from: <http://synderfiltration.com/learning-center/articles/introduction-to-membranes/membrane-materials-organic-inorganic/>.
18. Zahid, M., et al., *A Comprehensive Review on Polymeric Nano-Composite Membranes for Water Treatment*. Journal of Membrane Science & Technology, 2018. **08**(01).
19. Liu, F., et al., *Progress in the production and modification of PVDF membranes*. Journal of Membrane Science, 2011. **375**(1-2): p. 1-27.
20. Arkema, *High Performance Choice for Industrial Membranes*. 2015.
21. Pfenning, A., *Kirk-Othmer Encyclopedia of Chemical Technology*. 1995: Weinheim. p. 1022-1022.
22. Görlitz Von, M., et al., *Struktur und Eigenschaften von Polyvinylfluorid (PVF) und Polyvinylidenfluorid (PVF2)*. Die Angewandte Makromolekulare Chemie, 1973. **29**(1): p. 137-162.

23. Drobný, J., *Fluoroplastics*. 2006: Rapra Technology Limited.
24. Li, M., et al., *Revisiting the delta-phase of poly(vinylidene fluoride) for solution-processed ferroelectric thin films*. Nat Mater, 2013. **12**(5): p. 433-8.
25. Zheng, J., et al., *Polymorphism Control of Poly(vinylidene fluoride) through Electrospinning*. Macromolecular Rapid Communications, 2007. **28**(22): p. 2159-2162.
26. Martins, P., A.C. Lopes, and S. Lanceros-Mendez, *Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications*. Progress in Polymer Science, 2014. **39**(4): p. 683-706.
27. Sophie, R., M.K. Lynn, and J.L. H., *Molecular weight dependent of the crystallization kinetics of poly(vinylidene fluoride)*. Polymer Engineering & Science, 1992. **32**(17): p. 1300-1308.
28. Wang, X., et al., *Formation mechanism and crystallization of poly(vinylidene fluoride) membrane via immersion precipitation method*. Desalination, 2009. **236**(1-3): p. 170-178.
29. Cheng, L.-P., *Effect of Temperature on the Formation of Microporous PVDF Membranes by Precipitation from 1-Octanol/DMF/PVDF and Water/DMF/PVDF Systems*. Macromolecules, 1999. **32**(20): p. 6668-6674.
30. Lin, D.-J., et al., *Strong effect of precursor preparation on the morphology of semicrystalline phase inversion poly(vinylidene fluoride) membranes*. Journal of Membrane Science, 2006. **274**(1-2): p. 64-72.
31. Wang, X., et al., *Morphology and Formation Mechanism of Poly(Vinylidene Fluoride) Membranes Prepared with Immerse Precipitation: Effect of Dissolving Temperature*. Journal of Macromolecular Science, Part B, 2009. **48**(4): p. 696-709.
32. Liu, J., X.-L. Lu, and C.-R. Wu, *Effect of annealing conditions on crystallization behavior and mechanical properties of NIPS poly(vinylidene fluoride) hollow fiber membranes*. Journal of Applied Polymer Science, 2013. **129**(3): p. 1417-1425.
33. Haponska, M., et al., *PVDF Membrane Morphology—Influence of Polymer Molecular Weight and Preparation Temperature*. Polymers, 2017. **9**(12).
34. Liu, J., X. Lu, and C. Wu, *Effect of Preparation Methods on Crystallization Behavior and Tensile Strength of Poly(vinylidene fluoride) Membranes*. Membranes (Basel), 2013. **3**(4): p. 389-405.
35. Kim, J.F., et al., *Thermally induced phase separation and electrospinning methods for emerging membrane applications: A review*. AIChE Journal, 2016. **62**(2): p. 461-490.

36. Li, X., et al., *Effects of mixed diluent compositions on poly(vinylidene fluoride) membrane morphology in a thermally induced phase-separation process*. Journal of Applied Polymer Science, 2008. **107**(6): p. 3630-3637.
37. Su, Y., et al., *Preparation of PVDF Membranes via TIPS Method: The Effect of Mixed Diluents on Membrane Structure and Mechanical Property*. Journal of Macromolecular Science, Part A, 2007. **44**(3): p. 305-313.
38. Cui, Z., et al., *Crystalline polymorphism in poly(vinylidenefluoride) membranes*. Progress in Polymer Science, 2015. **51**: p. 94-126.
39. Nishiyama, T., et al., *Effect of solvents on the crystal formation of poly(vinylidene fluoride) film prepared by a spin-coating process*. Polymer Journal, 2017. **49**(3): p. 319-325.
40. McKeen, L.W., *Chapter 11 - Fluoropolymers*, in *Fatigue and Tribological Properties of Plastics and Elastomers (Second Edition)*. 2010, William Andrew Publishing: Oxford. p. 249-264.
41. Teng, H., *Overview of the Development of the Fluoropolymer Industry*. Applied Sciences, 2012. **2**(2): p. 496-512.
42. Hoa, S.V. and P. Ouellette, *Stress corrosion cracking of poly(vinylidene fluoride) in sodium hydroxide*. Polymer Engineering & Science, 1983. **23**(4): p. 202-205.
43. Komaki, Y. and H. Otsu, *Observation of nuclear track development in polyvinylidene fluoride with several etchants*. Journal of Electron Microscopy, 1981. **30**(4): p. 292-297.
44. Kise, H. and H. Ogata, *PHASE TRANSFER CATALYSIS IN DEHYDROFLUORINATION OF POLY(VINYLLIDENE FLUORIDE) BY AQUEOUS SODIUM HYDROXIDE SOLUTIONS*. Journal of polymer science. Part A-1, Polymer chemistry, 1983. **21**(12): p. 3443-3451.
45. Shinohara, H., *FLUORINATION OF POLYHYDROFLUOROETHYLENES - 2. FORMATION OF PERFLUOROALKYL CARBOXYLIC ACIDS ON THE SURFACE REGION OF POLY(VINYLLIDENE FLUORIDE) FILM BY OXYFLUORINATION, FLUORINATION, AND HYDROLYSIS*. J Polym Sci Polym Chem Ed, 1979. **17**(5): p. 1543-1556.
46. Komaki, Y., *Growth of fine holes by the chemical etching of fission tracks in polyvinylidene fluoride*. Nuclear Tracks, 1979. **3**(1-2): p. 33-44.

47. Rabuni, M.F., et al., *Effects of Alkaline Environments at Mild Conditions on the Stability of PVDF Membrane: An Experimental Study*. Industrial & Engineering Chemistry Research, 2013. **52**(45): p. 15874-15882.
48. Wegener, M., W. K unstler, and R. Gerhard-Multhaupt, *Poling behavior and optical absorption of partially dehydrofluorinated and uniaxially stretched polyvinylidene fluoride*. Ferroelectrics, 2006. **336**: p. 3-8.
49. Furusho, N., T. Komatsu, and T. Nakagawa, *A study of the thermal degradation of several halogen containing polymers by torsional braid analysis*. Bulletin of the Chemical Society of Japan, 1974. **47**(7): p. 1573-1577.
50. Biswas, A., et al., *Comparison of the thermal stability of the α , β and γ phases in poly(vinylidene fluoride) based on in situ thermal Fourier transform infrared spectroscopy*. Phase Transitions, 2017: p. 1-9.
51. Benzinger, W.D., B.S. Parekh, and J.L. Eichelberger, *High Temperature Ultrafiltration With Kynar  Poly(Vinylidene Fluoride) Membranes*. Separation Science and Technology, 1980. **15**(4): p. 1193-1204.
52. Simona, *Product Information PVDF*, ERIKS, Editor. 1998, ERIKS.
53. Crompton, T.R., *Physical Testing of Plastics*. 2012: Smithers Rapra.
54. Enzo, G., *Semi-crystalline fluorinated polymers*. Polymer International, 2001. **50**(1): p. 10-26.
55. Bottino, A., et al., *Solubility parameters of poly(vinylidene fluoride)*. Journal of Polymer Science Part B: Polymer Physics, 1988. **26**(4): p. 785-794.
56. Kang, G.-d. and Y.-m. Cao, *Application and modification of poly(vinylidene fluoride) (PVDF) membranes – A review*. Journal of Membrane Science, 2014. **463**: p. 145-165.
57. Ji, J., et al., *Poly(vinylidene fluoride) (PVDF) membranes for fluid separation*. Reactive and Functional Polymers, 2015. **86**: p. 134-153.
58. Munari, S., A. Bottino, and G. Capannelli, *Casting and performance of polyvinylidene fluoride based membranes*. Journal of Membrane Science, 1983. **16**: p. 181-193.
59. Dickey, C.A. and J.E. Mcdaniel, *Method of producing spherical thermoplastic particles*. 1975, Google Patents.
60. Ramsey, T.H., et al., *Composite porous materials and methods of making and using the same*. 2010, Google Patents.
61. Apel, P., *Track etching technique in membrane technology*. Radiation Measurements, 2001. **34**(1): p. 559-566.

62. Sartowska, B.A., *Nanopores with controlled profiles in track-etched membranes*. Nukleonika, 2012. **57**(4): p. 575-579.
63. Wang, X. and B.S. Hsiao, *Electrospun nanofiber membranes*. Current Opinion in Chemical Engineering, 2016. **12**: p. 62-81.
64. Ahmed, F.E., B.S. Lalia, and R. Hashaikh, *A review on electrospinning for membrane fabrication: Challenges and applications*. Desalination, 2015. **356**: p. 15-30.
65. Zhao, Z., et al., *Preparation and properties of electrospun poly(vinylidene fluoride) membranes*. Journal of Applied Polymer Science, 2005. **97**(2): p. 466-474.
66. Gee, S., B. Johnson, and A.L. Smith, *Optimizing electrospinning parameters for piezoelectric PVDF nanofiber membranes*. Journal of Membrane Science, 2018. **563**: p. 804-812.
67. Russo, F., et al., *Innovative Poly (Vinylidene Fluoride)(PVDF) Electrospun Nanofiber Membrane Preparation Using DMSO as a Low Toxicity Solvent*. Membranes, 2020. **10**(3): p. 36.
68. Wang, S., et al., *Fabrication of microporous membranes from melt extruded polypropylene precursor films via stretching: Effect of annealing*. Chinese Journal of Polymer Science, 2015. **33**(7): p. 1028-1037.
69. Charcosset, C., *Membrane Processes in Biotechnology and Pharmaceuticals*. 2012: Elsevier Science.
70. Zeman, *Microfiltration and Ultrafiltration: Principles and Applications*. 1996: Taylor & Francis.
71. Wang, B., et al., *Porous membranes prepared by a combined crystallisation and diffusion (CCD) method: Study on formation mechanisms*. Journal of Membrane Science, 2018. **548**: p. 136-148.
72. Wang, B., J. Ji, and K. Li, *Crystal nuclei templated nanostructured membranes prepared by solvent crystallization and polymer migration*. Nat Commun, 2016. **7**: p. 12804.
73. Ladewig, B. and M.N.Z. Al-Shaeli, *Fundamentals of Membrane Processes*, in *Fundamentals of Membrane Bioreactors*. 2017. p. 13-37.
74. Mulder, M. and J. Mulder, *Basic Principles of Membrane Technology*. 1996: Springer Netherlands.
75. Koops, G., *Preparation and Characterisation of Micro- and Ultrafiltration Membranes*. MEMBRANE PROCESSES. Vol. II. 2010: EOLSS Publications.

76. Thakur, V.K. and M.K.U.h.b.g.c.u.b.i.z. Thakur, *Handbook of Polymers for Pharmaceutical Technologies, Processing and Applications*. 2015: Wiley.
77. Garcia, J.U., et al., *Mechanisms of Asymmetric Membrane Formation in Nonsolvent-Induced Phase Separation*. ACS Macro Letters, 2020. **9**(11): p. 1617-1624.
78. Shah, V., B. Wang, and K. Li, *Blending modification to porous polyvinylidene fluoride (PVDF) membranes prepared via combined crystallisation and diffusion (CCD) technique*. Journal of Membrane Science, 2021. **618**: p. 118708.
79. Lloyd, D.R., K.E. Kinzer, and H.S. Tseng, *Microporous membrane formation via thermally induced phase separation. I. Solid-liquid phase separation*. Journal of Membrane Science, 1990. **52**(3): p. 239-261.
80. Gu, M., et al., *Formation of poly(vinylidene fluoride) (PVDF) membranes via thermally induced phase separation*. Desalination, 2006. **192**(1-3): p. 160-167.
81. Jung, J.T., et al., *Understanding the non-solvent induced phase separation (NIPS) effect during the fabrication of microporous PVDF membranes via thermally induced phase separation (TIPS)*. Journal of Membrane Science, 2016. **514**: p. 250-263.
82. Stropnik, C., L. Germič, and B. Žerjal, *Morphology variety and formation mechanisms of polymeric membranes prepared by wet phase inversion*. Journal of Applied Polymer Science, 1996. **61**(10): p. 1821-1830.
83. Bottino, A., et al., *The formation of microporous polyvinylidene difluoride membranes by phase separation*. Journal of Membrane Science, 1991. **57**(1): p. 1-20.
84. Yeow, M.L., Y.T. Liu, and K. Li, *Morphological study of poly(vinylidene fluoride) asymmetric membranes: Effects of the solvent, additive, and dope temperature*. Journal of Applied Polymer Science, 2004. **92**(3): p. 1782-1789.
85. Li, Q., Z.L. Xu, and L.Y. Yu, *Effects of mixed solvents and PVDF types on performances of PVDF microporous membranes*. Journal of Applied Polymer Science, 2009. **115**(4): p. 2277-2287.
86. Munari, S., A. Bottino, and G. Capannelli, *Casting and performance of polyvinylidene fluoride based membranes*. Journal of Membrane Science, 1983. **16**(C): p. 181-193.
87. Fontananova, E., et al., *Effect of additives in the casting solution on the formation of PVDF membranes*. Desalination, 2006. **192**(1-3): p. 190-197.
88. Kong, J. and K. Li, *Preparation of PVDF hollow-fiber membranes via immersion precipitation*. Journal of Applied Polymer Science, 2001. **81**(7): p. 1643-1653.

89. Wang, D., K. Li, and W.K. Teo, *Porous PVDF asymmetric hollow fiber membranes prepared with the use of small molecular additives*. Journal of Membrane Science, 2000. **178**(1-2): p. 13-23.
90. Tomaszewska, M., *Preparation and properties of flat-sheet membranes from poly(vinylidene fluoride) for membrane distillation*. Desalination, 1996. **104**(1-2): p. 1-11.
91. Bottino, A., et al., *High performance ultrafiltration membranes cast from LiCl doped solutions*. Desalination, 1988. **68**(2-3): p. 167-177.
92. Yeow, M.L., Y. Liu, and K. Li, *Preparation of porous PVDF hollow fibre membrane via a phase inversion method using lithium perchlorate (LiClO₄) as an additive*. Journal of Membrane Science, 2005. **258**(1-2): p. 16-22.
93. Shih, H.C., Y.S. Yeh, and H. Yasuda, *Morphology of microporous poly(vinylidene fluoride) membranes studied by gas permeation and scanning electron microscopy*. Journal of Membrane Science, 1990. **50**(3): p. 299-317.
94. Khayet, M., et al., *Study on the effect of a non-solvent additive on the morphology and performance of ultrafiltration hollow-fiber membranes*. Desalination, 2002. **148**(1-3): p. 321-327.
95. Khayet, M. and T. Matsuura, *Preparation and characterization of polyvinylidene fluoride membranes for membrane distillation*. Industrial and Engineering Chemistry Research, 2001. **40**(24): p. 5710-5718.
96. Wang, D., K. Li, and W.K. Teo, *Preparation and characterization of polyvinylidene fluoride (PVDF) hollow fiber membranes*. Journal of Membrane Science, 1999. **163**(2): p. 211-220.
97. Deshmukh, S.P. and K. Li, *Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fibre membranes*. Journal of Membrane Science, 1998. **150**(1): p. 75-85.
98. Uragami, T., Y. Naito, and M. Sugihara, *Studies on synthesis and permeability of special polymer membranes*. Polymer Bulletin, 1981. **4**(10): p. 617-622.
99. Kestling, R.E., *Synthetic Polymeric Membranes: A structural Perspective*. John Wiley & Sons Inc., 1985.
100. Cheng, L.P., et al., *Formation of particulate microporous poly(vinylidene fluoride) membranes by isothermal immersion precipitation from the 1-octanol/dimethylformamide/poly(vinylidene fluoride) system*. Polymer, 1999. **40**(9): p. 2395-2403.

101. Sukitpaneenit, P. and T.S. Chung, *Molecular elucidation of morphology and mechanical properties of PVDF hollow fiber membranes from aspects of phase inversion, crystallization and rheology*. Journal of Membrane Science, 2009. **340**(1-2): p. 192-205.
102. Wang, X., et al., *Effect of coagulation bath temperature on formation mechanism of poly(vinylidene fluoride) membrane*. Journal of Applied Polymer Science, 2008. **110**(3): p. 1656-1663.
103. Drioli, E., L. Giorno, and E. Fontananova, *Comprehensive Membrane Science and Engineering*. 2017: Elsevier Science.
104. Su, Y., et al., *PVDF membrane formation via thermally induced phase separation*. Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 2007. **44**(1): p. 99-104.
105. Kim, S.S. and D.R. Lloyd, *Thermodynamics of polymer/diluent systems for thermally induced phase separation: 3. Liquid-liquid phase separation systems*. Polymer, 1992. **33**(5): p. 1047-1057.
106. Ji, G.L., et al., *Preparation of porous PVDF membrane via thermally induced phase separation with diluent mixture of DBP and DEHP*. Journal of Applied Polymer Science, 2007. **105**(3): p. 1496-1502.
107. Gu, M., et al., *Crystallization behavior of PVDF in PVDF-DMP system via thermally induced phase separation*. Journal of Applied Polymer Science, 2006. **102**(4): p. 3714-3719.
108. Shi, F., et al., *Effect of quenching temperatures on the morphological and crystalline properties of PVDF and PVDF-TiO₂ hybrid membranes*. Journal of the Taiwan Institute of Chemical Engineers, 2012. **43**(6): p. 980-988.
109. Caneba, G.T. and D.S. Soong, *Polymer membrane formation through the thermal-inversion process. 1. Experimental study of membrane structure formation*. Macromolecules, 1985. **18**(12): p. 2538-2545.
110. Tsai, F.J. and J.M. Torkelson, *The roles of phase separation mechanism and coarsening in the formation of poly(methyl methacrylate) asymmetric membranes*. Macromolecules, 1990. **23**(3): p. 775-784.
111. Matsuyama, H., et al., *Effects of thermal history on anisotropic and asymmetric membranes formed by thermally induced phase separation*. Journal of Membrane Science, 1998. **142**(1): p. 27-42.

112. Matsuyama, H., S. Berghmans, and D.R. Lloyd, *Formation of anisotropic membranes via thermally induced phase separation*. Polymer, 1999. **40**(9): p. 2289-2301.
113. Matsuyama, H., et al., *Structure control of anisotropic and asymmetric polypropylene membrane prepared by thermally induced phase separation*. Journal of Membrane Science, 2000. **179**(1): p. 91-100.
114. Caplan, M.R., et al., *Formation of microporous Teflon® PFA membranes via thermally induced phase separation*. Journal of Membrane Science, 1997. **130**(1): p. 219-237.
115. Jin, T.-T., Z.-P. Zhao, and K.-C. Chen, *Preparation of a poly(vinyl chloride) ultrafiltration membrane through the combination of thermally induced phase separation and non-solvent-induced phase separation*. Journal of Applied Polymer Science, 2016. **133**(5): p. n/a-n/a.
116. Lee, J., et al., *Effect of PVP, lithium chloride, and glycerol additives on PVDF dual-layer hollow fiber membranes fabricated using simultaneous spinning of TIPS and NIPS*. Macromolecular Research, 2015. **23**(3): p. 291-299.
117. Liu, J., et al., *Preparation and properties of poly (vinylidene fluoride) membranes via the low temperature thermally induced phase separation method*. Journal of Polymer Research, 2014. **21**(10).
118. Xiao, T., et al., *Fabrication and characterization of novel asymmetric polyvinylidene fluoride (PVDF) membranes by the nonsolvent thermally induced phase separation (NTIPS) method for membrane distillation applications*. Journal of Membrane Science, 2015. **489**: p. 160-174.
119. Li, Q., Z.-L. Xu, and L.-Y. Yu, *Effects of mixed solvents and PVDF types on performances of PVDF microporous membranes*. Journal of Applied Polymer Science, 2010. **115**(4): p. 2277-2287.
120. Wang, D., K. Li, and W.K. Teo, *Porous PVDF asymmetric hollow fiber membranes prepared with the use of small molecular additives*. Journal of Membrane Science, 2000. **178**(1): p. 13-23.
121. Khayet, M., et al., *Preparation and characterization of polyvinylidene fluoride hollow fiber membranes for ultrafiltration*. Polymer, 2002. **43**(14): p. 3879-3890.
122. Khayet, M., et al., *Study on the effect of a non-solvent additive on the morphology and performance of ultrafiltration hollow-fiber membranes*. Desalination, 2002. **148**(1): p. 321-327.

123. Wang, X., et al., *Effect of protein on PVDF ultrafiltration membrane fouling behavior under different pH conditions: interface adhesion force and XDLVO theory analysis*. Frontiers of Environmental Science & Engineering, 2016. **10**(4): p. 1-11.
124. Nunes, S.P. and K.V. Peinemann, *Ultrafiltration membranes from PVDF/PMMA blends*. Journal of Membrane Science, 1992. **73**(1): p. 25-35.
125. Lv, J., et al., *Improvement of antifouling performances for modified PVDF ultrafiltration membrane with hydrophilic cellulose nanocrystal*. Applied Surface Science, 2018. **440**: p. 1091-1100.
126. Yuliwati, E. and A.F. Ismail, *Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced wastewater treatment*. Desalination, 2011. **273**(1): p. 226-234.
127. Cao, X., et al., *Effect of TiO₂ nanoparticle size on the performance of PVDF membrane*. Applied Surface Science, 2006. **253**(4): p. 2003-2010.
128. Yan, L., Y.S. Li, and C.B. Xiang, *Preparation of poly(vinylidene fluoride)(pvdf) ultrafiltration membrane modified by nano-sized alumina (Al₂O₃) and its antifouling research*. Polymer, 2005. **46**(18): p. 7701-7706.
129. Yu, L.-Y., et al., *Preparation and characterization of PVDF–SiO₂ composite hollow fiber UF membrane by sol–gel method*. Journal of Membrane Science, 2009. **337**(1): p. 257-265.
130. Wei, Y., et al., *Effect of TiO₂ nanowire addition on PVDF ultrafiltration membrane performance*. Desalination, 2011. **272**(1): p. 90-97.
131. Wang, Z., et al., *Novel GO-blended PVDF ultrafiltration membranes*. Desalination, 2012. **299**: p. 50-54.
132. Chang, X., et al., *Exploring the synergetic effects of graphene oxide (GO) and polyvinylpyrrolidone (PVP) on poly(vinylidene fluoride) (PVDF) ultrafiltration membrane performance*. Applied Surface Science, 2014. **316**: p. 537-548.
133. Safarpour, M., A. Khataee, and V. Vatanpour, *Preparation of a Novel Polyvinylidene Fluoride (PVDF) Ultrafiltration Membrane Modified with Reduced Graphene Oxide/Titanium Dioxide (TiO₂) Nanocomposite with Enhanced Hydrophilicity and Antifouling Properties*. Industrial & Engineering Chemistry Research, 2014. **53**(34): p. 13370-13382.
134. Zhao, C., et al., *Effect of graphene oxide concentration on the morphologies and antifouling properties of PVDF ultrafiltration membranes*. Journal of Environmental Chemical Engineering, 2013. **1**(3): p. 349-354.

135. Ayyaru, S., T.T.L. Dinh, and Y.-H. Ahn, *Enhanced antifouling performance of PVDF ultrafiltration membrane by blending zinc oxide with support of graphene oxide nanoparticle*. Chemosphere, 2020. **241**: p. 125068.
136. Xu, Z., et al., *Photocatalytic antifouling PVDF ultrafiltration membranes based on synergy of graphene oxide and TiO₂ for water treatment*. Journal of Membrane Science, 2016. **520**: p. 281-293.
137. Tan, Y.H., et al., *Decolourization of aerobically treated palm oil mill effluent (AT-POME) using polyvinylidene fluoride (PVDF) ultrafiltration membrane incorporated with coupled zinc-iron oxide nanoparticles*. Chemical Engineering Journal, 2017. **308**: p. 359-369.
138. Ma, C., et al., *Graphene oxide-polyethylene glycol incorporated PVDF nanocomposite ultrafiltration membrane with enhanced hydrophilicity, permeability, and antifouling performance*. Chemosphere, 2020. **253**: p. 126649.
139. Zeng, G., et al., *Preparation and characterization of a novel PVDF ultrafiltration membrane by blending with TiO₂-HNTs nanocomposites*. Applied Surface Science, 2016. **371**: p. 624-632.
140. Yu, H., et al., *Hydrothermal carbon nanospheres assisted-fabrication of PVDF ultrafiltration membranes with improved hydrophilicity and antifouling performance*. Separation and Purification Technology, 2020. **247**: p. 116889.
141. Arefi-Oskoui, S., V. Vatanpour, and A. Khataee, *Development of a novel high-flux PVDF-based ultrafiltration membrane by embedding Mg-Al nanolayered double hydroxide*. Journal of Industrial and Engineering Chemistry, 2016. **41**: p. 23-32.
142. Tofighy, M.A., T. Mohammadi, and M.H. Sadeghi, *High-flux PVDF/PVP nanocomposite ultrafiltration membrane incorporated with graphene oxide nanoribbons with improved antifouling properties*. Journal of Applied Polymer Science, 2021. **138**(4): p. 49718.
143. Zhou, A., et al., *Abatement of sulfadiazine in water under a modified ultrafiltration membrane (PVDF-PVP-TiO₂-dopamine) filtration-photocatalysis system*. Separation and Purification Technology, 2020. **234**: p. 116099.
144. Hong, J. and Y. He, *Polyvinylidene fluoride ultrafiltration membrane blended with nano-ZnO particle for photo-catalysis self-cleaning*. Desalination, 2014. **332**(1): p. 67-75.

145. Liu, Q., et al., *Comparing the antifouling effects of activated carbon and TiO₂ in ultrafiltration membrane development*. Journal of Colloid and Interface Science, 2018. **515**: p. 109-118.
146. Zhu, J., et al., *PVDF mixed matrix ultrafiltration membrane incorporated with deformed rebar-like Fe₃O₄-palygorskite nanocomposites to enhance strength and antifouling properties*. Journal of Membrane Science, 2020. **612**: p. 118467.
147. Abdollahi, E., et al., *Application of Mg-Al LDH nanoparticles to enhance flux, hydrophilicity and antifouling properties of PVDF ultrafiltration membrane: Experimental and modeling studies*. Separation and Purification Technology, 2021. **257**: p. 117931.
148. Teow, Y.H., et al., *Hydroxyl functionalized PVDF-TiO₂ ultrafiltration membrane and its antifouling properties*. Journal of Applied Polymer Science, 2015. **132**(21).
149. Safarpour, M., A. Khataee, and V. Vatanpour, *Effect of reduced graphene oxide/TiO₂ nanocomposite with different molar ratios on the performance of PVDF ultrafiltration membranes*. Separation and Purification Technology, 2015. **140**: p. 32-42.
150. Shao, L., et al., *A facile strategy to enhance PVDF ultrafiltration membrane performance via self-polymerized polydopamine followed by hydrolysis of ammonium fluotitanate*. Journal of Membrane Science, 2014. **461**: p. 10-21.
151. Liu, X., et al., *A novel PVDF/PFSA-g-GO ultrafiltration membrane with enhanced permeation and antifouling performances*. Separation and Purification Technology, 2020. **233**: p. 116038.
152. Fu, X., et al., *Sulfonated poly(α,β,β -trifluorostyrene)-doped PVDF ultrafiltration membrane with enhanced hydrophilicity and antifouling property*. Journal of Membrane Science, 2020. **603**: p. 118046.
153. Liu, H., et al., *Hydraulic power and electric field combined antifouling effect of a novel conductive poly(aminoanthraquinone)/reduced graphene oxide nanohybrid blended PVDF ultrafiltration membrane*. Journal of Materials Chemistry A, 2015. **3**(40): p. 20277-20287.
154. Zhao, X. and C. He, *Efficient Preparation of Super Antifouling PVDF Ultrafiltration Membrane with One Step Fabricated Zwitterionic Surface*. ACS Applied Materials & Interfaces, 2015. **7**(32): p. 17947-17953.
155. Thankappan, H., et al., *Development of PVDF Ultrafiltration Membrane with Zwitterionic Block Copolymer Micelles as a Selective Layer*. Membranes, 2019. **9**(8).

156. Wang, P., et al., *Enhanced Separation Performance of PVDF/PVP-g-MMT Nanocomposite Ultrafiltration Membrane Based on the NVP-Grafted Polymerization Modification of Montmorillonite (MMT)*. Langmuir, 2012. **28**(10): p. 4776-4786.
157. Wang, H., X. Zhao, and C. He, *Enhanced antifouling performance of hybrid PVDF ultrafiltration membrane with the dual-mode SiO₂-g-PDMS nanoparticles*. Separation and Purification Technology, 2016. **166**: p. 1-8.
158. Saini, B., et al., *A novel stimuli-responsive and fouling resistant PVDF ultrafiltration membrane prepared by using amphiphilic copolymer of poly(vinylidene fluoride) and Poly(2-N-morpholino)ethyl methacrylate*. Journal of Membrane Science, 2020. **603**: p. 118047.
159. Wang, S., et al., *PVDF ultrafiltration membranes of controlled performance via blending PVDF-g-PEGMA copolymer synthesized under different reaction times*. Frontiers of Environmental Science & Engineering, 2017. **12**(2): p. 3.
160. Liu, B., et al., *High performance ultrafiltration membrane composed of PVDF blended with its derivative copolymer PVDF-g-PEGMA*. Journal of Membrane Science, 2013. **445**: p. 66-75.
161. Wu, T., et al., *Facile and low-cost approach towards a PVDF ultrafiltration membrane with enhanced hydrophilicity and antifouling performance via graphene oxide/water-bath coagulation*. RSC Advances, 2015. **5**(11): p. 7880-7889.
162. Zhao, Z., et al., *High performance ultrafiltration membrane based on modified chitosan coating and electrospun nanofibrous PVDF scaffolds*. Journal of Membrane Science, 2012. **394-395**: p. 209-217.
163. Fontananova, E., et al., *Effect of additives in the casting solution on the formation of PVDF membranes*. Desalination, 2006. **192**(1): p. 190-197.
164. Li, H.-B., et al., *Effects of Additives on the Morphology and Performance of PPTA/PVDF in Situ Blend UF Membrane*. Polymers, 2014. **6**(6).
165. Arahman, N., et al., *Improving Water Permeability of Hydrophilic PVDF Membrane Prepared via Blending with Organic and Inorganic Additives for Humic Acid Separation*. Molecules (Basel, Switzerland), 2019. **24**(22): p. 4099.
166. Zhang, P.-Y., H. Yang, and Z.-L. Xu, *Preparation of Polyvinylidene Fluoride (PVDF) Membranes via Nonsolvent Induced Phase Separation Process using a Tween 80 and H₂O Mixture As an Additive*. Industrial & Engineering Chemistry Research, 2012. **51**(11): p. 4388-4396.

167. Razzaghi, M.H., et al., *Investigation of the effect of coagulation bath composition on PVDF/CA membrane by evaluating critical flux and antifouling properties in lab-scale submerged MBR*. Water and Environment Journal, 2018. **32**(3): p. 366-376.
168. Wu, Q., et al., *Improving the Performance of PVDF/PVDF-g-PEGMA Ultrafiltration Membranes by Partial Solvent Substitution with Green Solvent Dimethyl Sulfoxide during Fabrication*. ACS Omega, 2019. **4**(22): p. 19799-19807.
169. Loh, C.H. and R. Wang, *Effects of Additives and Coagulant Temperature on Fabrication of High Performance PVDF/Pluronic F127 Blend Hollow Fiber Membranes via Nonsolvent Induced Phase Separation*. Chinese Journal of Chemical Engineering, 2012. **20**(1): p. 71-79.
170. Abed, M.M., et al., *Economical production of PVDF-g-POEM for use as a blend in preparation of PVDF based hydrophilic hollow fibre membranes*. Separation and Purification Technology, 2013. **106**: p. 47-55.
171. Wang, S., et al., *Non-woven PET fabric reinforced and enhanced the performance of ultrafiltration membranes composed of PVDF blended with PVDF-g-PEGMA for industrial applications*. Applied Surface Science, 2018. **435**: p. 1072-1079.
172. DUPONT. *IntegraPacTM Ultrafiltration Modules Product Data Sheet*. 02 June 2021]; Available from: <https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/45-D01162-en.pdf>.
173. DUPONT. *IntegraFluxTM Ultrafiltration Modules Product Data Sheet*. 02 June 2021]; Available from: <https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/45-D01048-en.pdf>.
174. Suez. *ZeeWeed immersed ultrafiltration model ZW1000 fact sheet*. 02 June 2021]; Available from: <https://www.suezwatertechnologies.com/products/ultrafiltration/zeeweed-1000-membrane>.
175. Suez. *ZeeWeed pressured ultrafiltration model ZW1500*. Available from: <https://www.suezwatertechnologies.com/products/ultrafiltration/zeeweed-1500-membrane>.
176. Company, H.N.G. *Capillary Ultrafiltration Module HYDRAcap® MAX 80*. 02 June 2021]; Available from: <https://membranes.com/solutions/products/uf/hydracap-max/>.

177. KOCH. *PURON® MP Hollow Fiber Cartridge Datasheet*. 02 June 2021]; Available from: <https://www.kochseparation.com/wp-content/uploads/2020/10/puron-mp-8081-pressurized-hollow-fiber-uf-modules.pdf>.
178. QUA®. *EnviQ® Submerged Ultrafiltration Membranes*. 02 June 2021]; Available from: <https://quagroup.com/wp-content/uploads/QUA-EnviQ-Data-Sheet-1.pdf>.
179. TORAY. *MEMBRAY™ submerged Flat sheet Membrane Modules for MBR*. 02 June 2021]; Available from: <https://pureaqua.com/content/pdf/membray-submerged-flat-sheet-membrane-modules-for-mbr-tmr140-series-data-sheet.pdf>.
180. Xie, W., et al., *Using the Green Solvent Dimethyl Sulfoxide To Replace Traditional Solvents Partly and Fabricating PVC/PVC-g-PEGMA Blended Ultrafiltration Membranes with High Permeability and Rejection*. Industrial & Engineering Chemistry Research, 2019. **58**(16): p. 6413-6423.
181. Funk, C.V., et al., *Diluent crystal alignment in the formation of membranes via liquid–solid thermally induced phase separation*. Journal of Porous Materials, 2008. **16**(4): p. 453-458.
182. Kim, S.S., et al., *Microporous membrane formation via thermally-induced phase separation. V. Effect of diluent mobility and crystallization on the structure of isotactic polypropylene membranes*. Journal of Membrane Science, 1991. **64**(1): p. 41-53.
183. Liang, H.-Q., et al., *Polar polymer membranes via thermally induced phase separation using a universal crystallizable diluent*. Journal of Membrane Science, 2013. **446**: p. 482-491.
184. Rozelle, L., et al., *Phase inversion membranes*. Encyclopedia of Separation Science, M. Mulder, Editor, Academic Press, NY, 2000: p. 3331-3346.
185. van de Witte, P., et al., *Phase separation processes in polymer solutions in relation to membrane formation*. Journal of Membrane Science, 1996. **117**(1): p. 1-31.
186. Burghardt, W.R., *Phase diagrams for binary polymer systems exhibiting both crystallization and limited liquid-liquid miscibility*. Macromolecules, 1989. **22**(5): p. 2482-2486.
187. Li, S.G., et al., *Physical Gelation of Amorphous Polymers in a Mixture of Solvent and Nonsolvent*. Macromolecules, 1996. **29**(6): p. 2053-2059.
188. Ji, J., *Poly(vinylidene fluoride) Membranes*, in *Department of Chemical Engineering*. 2016, Imperial College London: London.

3 Experimental Materials and Method

Each study mentioned in the subsequent chapters will have its own “Methodology” section, which is unique to it alone. However, the common materials and characterisation techniques that are used in two or more studies are mentioned in this section to avoid repetition in later sections.

3.1 Materials

Commercial PVDF (Kynar®K-761, MW = 440kDa, $\rho = 1.79 \text{ g.cm}^{-3}$) was purchased from Elf Atochem. Solvents such as DMSO (HPLC grade), Isobutanol (HPLC grade), n-hexane (GPR), and ethanol (Analar) were purchased from VWR, UK. DMSO was used as a solvent for PVDF in preparing the dope solutions. Isobutanol was used to prepare an isobutanol-water mixture to be used for liquid-liquid porometry. Ethanol and n-hexane were used in solvent exchange steps used for drying the membrane.

3.2 CCD membrane preparation

The casting and cooling conditions used in the CCD method are summarised in Table 3.1. The preparation of CCD membranes was carried out following a three-step process as illustrated earlier in Figure 2.9 in section 2.11. The three steps are summarised below.

Table 3.1. Operating conditions used in the CCD method

Condition	Value
Dope dissolution temperature	80°C
Casting thickness	0.5 mm
Temperature of the cooling plate	-30°C
Temperature of the casting plate	Room temperature
Cooling plate material and thickness	Aluminium, 6mm
Casting plate material and thickness	Aluminium, 6mm

- Step 1: Casting- The homogenous polymer dope is spread on an aluminium casting plate using a casting knife with 0.5 mm casting thickness. Appendix A shows the casting setup used.

- Step 2: Cooling- The casting plate is then placed on top of an aluminium cooling plate (maintained at -30°C). As soon as the two plates would come in contact, rapid dissipation of heat freezes the polymer cast layer (in <3s).
- Step 3: Leaching- The solidified polymer cast layer is finally immersed in an icy water bath to leach out the solvent molecules to obtain the porous membrane.

3.3 Membrane Characterisation

3.3.1 Scanning Electron Microscope (SEM)

The morphology of the membranes prepared was observed using SEM (LEO Gemini 1525 FEGSEM, Tokyo, Japan) (See Appendix B-1). For sample preparation, wet membrane samples were first subjected to two cycles of ethanol immersion, followed by two cycles of n-hexane immersion, with each immersion cycle lasting a period of 4 hours. After immersion, the membranes were dried out and used for SEM. The membrane cross-section samples were prepared by fracturing the dried membranes in liquid nitrogen. The prepared samples were finally gold-coated at 10nm thickness to make the surface electrically conductive, ready for SEM observation.

3.3.2 Liquid-Liquid Displacement Porometry (LLDP)

In this thesis, mean flow pore sizes have been used to characterise the separation performance of the membranes as opposed to the molecular weight cut-off (MWCO) experiments that are typically performed. The mean flow pore sizes were measured using a liquid-liquid displacement porometer (LLP 1500A, Porous Materials Inc., USA) (See Appendix B-2). A mixture of 1:1 (v/v) isobutanol-water was prepared, which separated into two equilibrated phases - an isobutanol-rich phase and a water-rich phase. The membranes were pre-wet with isobutanol-rich phase while the water-rich phase was used to push the wetting liquid out of the pores by application of pressure. At each step change in pressure, the permeate flux was measured. The pore sizes corresponding to the operating pressure P_i is given by Young-Laplace equation:

$$r_k = \frac{2 \cdot \gamma \cdot \cos\theta}{P_i} \quad \text{Equation 3.1}$$

In Equation 3.1, r_k is the pore radius, γ is the interfacial tension between the two liquids (1.7 mN/m) and θ is the contact angle of the wetting liquid on the membrane surface (taken as 0° due to complete spreading). The wet and dry flow curves obtained were then analysed by CapRep software to deduce the pore size distribution and the mean flow pore size of the sample [1]. It should be noted that a shape factor of 0.715 was used for the analysis. The pore size distribution hence obtained will provide a reasonable estimate about the membrane's rejection capabilities. The actual rejections will however depend the type of application and nature of solutes present.

The membrane porosity can also be calculated from the data obtained by the porometer using Hagen-Poiseuille equation [2-5]:

$$Q_i = \sum_{k=1}^i \frac{\pi P_i n_k r_k^4}{8 \mu l} \quad \text{Equation 3.2}$$

Equation 3.2 correlates the volumetric flowrate Q_i obtained at pressure P_i , with the number of pores that have then opened n_k , having a radius r_k . The dynamic viscosity μ is that of the pushing liquid while l is the active layer thickness of an asymmetric membrane or total membrane thickness of a symmetric membrane. CCD membranes are asymmetric, and the active layer is approximated to be $1/100^{\text{th}}$ of the total membrane thickness. Once the number of pores n_k are determined for pores of radius r_k , the membrane porosity φ , can be determined using Equation 3.3, where A_s is the area of membrane sample exposed.

$$\varphi = \frac{\sum n_k \pi r_k^2}{A_s} \quad \text{Equation 3.3}$$

5 specimens from different membrane sheets of each sample were used for measurement, and the average of mean flow pore sizes and membrane porosities reported.

3.3.3 Pure Water Permeance (PWP) measurement

The PWPs of the membranes were characterised using a 1000ml dead-end filtration cell (See Appendix B-3). Pure water was used as the feed liquid and the applied pressure difference was set at 1 bar. The permeance measurements were taken for a period of 20 mins and were calculated using the following formula:

$$PWP = \frac{J_w}{p} = \frac{V}{A \times \Delta t \times p} \quad \text{Equation 3.4}$$

In Equation 3.4, *PWP* is the pure water permeance (L.m⁻².hr⁻¹.bar⁻¹ or LMH.bar⁻¹), *J_w* is the pure water flux (L.m⁻².hr⁻¹ or LMH), *V* is the permeated volume (litres) in time Δt (hours), *A* is the active membrane area (m²), and *p* is the applied pressure difference (bar). 5 specimens from different membrane sheets of each sample were used for measurement, and the average of these values was reported as the PWP.

3.3.4 Membrane Mechanical Strength

Mechanical properties of the membranes were tested as per the standard method described in American Society for Testing and Materials (ASTM) D882 using a tensile testing machine, Lloyd EZ50 (See Appendix B-4). The gauge length and sample width were fixed at 50mm and 10mm respectively. A constant stretching rate of 10mm/min was applied to the samples. Before starting the measurement, the thickness of each sample was measured and recorded using the digital caliper. As the membrane was stretched, the tensile force was recorded by a transducer and parameters such as load applied, tensile strength, strain, and Young's modulus were calculated. For each sample, ten specimens were tested, and the average values were reported.

3.3.5 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The instrument used for this was Agilent Technologies Cary 630 FTIR Spectrometer (See Appendix B-5). The samples were placed on the diamond crystal and pressed using a compression rod before recording. All spectral data recorded were in the wavenumber range of 4000-600 cm⁻¹ with each spectrum generated being an average of the eight scans per sample with a resolution of 2cm⁻¹. For each sample, at least five specimens were analysed.

3.4 References

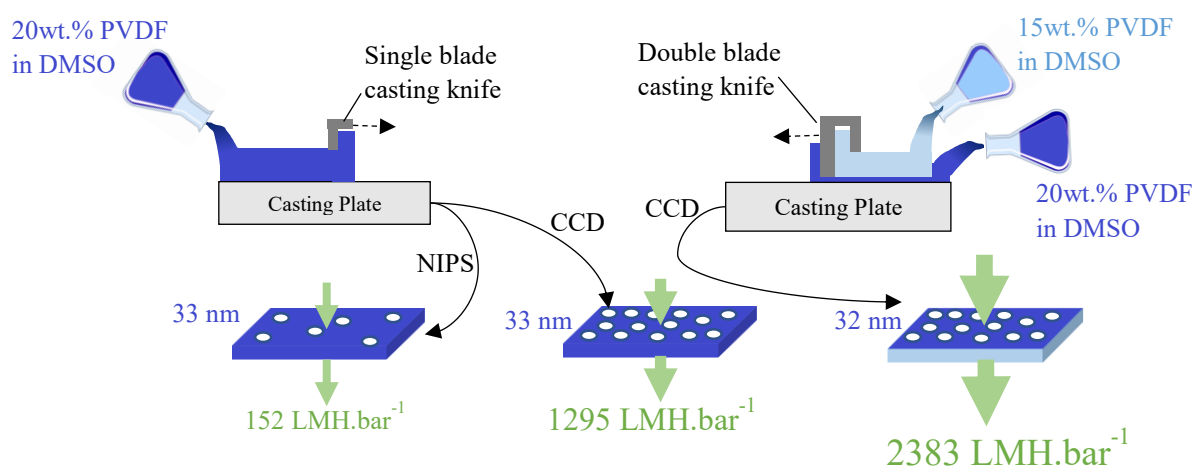
1. Jena, A. and K. Gupta, *Advances in Pore Structure Evaluation by Porometry*. Chemical Engineering & Technology, 2010. **33**(8): p. 1241-1250.
2. Calvo, J.I., et al., *Liquid-liquid displacement porometry to estimate the molecular weight cut-off of ultrafiltration membranes*. Desalination, 2011. **268**(1): p. 174-181.

3. Calvo, J.I., et al., *Comparison of liquid–liquid displacement porosimetry and scanning electron microscopy image analysis to characterise ultrafiltration track-etched membranes*. Journal of Membrane Science, 2004. **239**(2): p. 189-197.
4. Calvo, J.I., et al., *Comparison of pore size distributions from dextran retention tests and liquid-liquid displacement porosimetry*. Microporous and Mesoporous Materials, 2017. **250**: p. 170-176.
5. Peinador, R.I., et al., *Characterisation of polymeric UF membranes by liquid–liquid displacement porosimetry*. Journal of Membrane Science, 2010. **348**(1): p. 238-244.

4 Enhancement of permeation characteristics of PVDF-CCD membranes via a novel dual-casting technique

Abstract

The effect of polymer dope concentration on the membrane morphology has been well studied for mature fabrication techniques such as NIPS and TIPS. The CCD method which offers advantages over these traditional methods is still in its nascent stage and PVDF membranes prepared so far using this technique, have been made using only a single dope solution concentration. In this chapter, varied dope solution concentrations have been applied to CCD-PVDF membranes to study their effect on membrane morphology and investigate the range of achievable pore sizes and pure water permeances. The claim of superior permeation rates in CCD membranes over its NIPS counterparts was further validated by also fabricating and characterising NIPS membranes in parallel with CCD membranes at different dope solution concentrations. With the aim to enhance the permeation performance even further, a proof-of-concept study was then undertaken, by developing a novel but a simple dual-casting technique for making CCD membranes. Using this technique, one can tailor the specific properties of the separation and support layer of the membrane, by merely changing the dope concentrations of the two casted layers. The results showed that the concept is workable, and the pure water permeance of the membranes are higher by almost 15 times than the traditional NIPS membranes.



Keywords: PVDF membrane, Ultrafiltration, Permeance, Polymer concentration, Dual-layer

4.1 Introduction

There are many methods of membrane preparation as described above in section 2.6 and each one has its influencing factors that if controlled in a certain way can influence the membrane morphology. However, one that always influences the membrane morphology, irrespective of the preparation method, is the polymer dope concentration, as the membrane is ultimately constituted of the polymer that is loaded in the dope.

In a NIPS process, the dope solution concentration can affect the solvent-nonsolvent mutual diffusion rates which ultimately decides the composition path that will be followed before the phase separation is complete as was seen in Figure 2.5 in section 2.7.1 [1]. Liquid-liquid demixing can take place via two possible pathways- either through “instantaneous demixing” or through “delayed demixing” [1, 2]. “Instantaneous demixing” pathway produces more porous membranes with many macrovoids in its sub-layer, while the “delayed demixing” pathway produces membranes that are relative denser and have a sub-layer with a sponge-like or closed-cell morphology [2, 3]. Macrovoids weaken the mechanical properties of the membrane as they tend to collapse under pressure and therefore it is preferred if its formation can be avoided [2]. Increasing the concentration of the polymer dope has proven to be an effective strategy to avoid the “instantaneous demixing” route. A higher polymer dope has a higher solution viscosity which retards the solvent-nonsolvent mutual diffusion rates and thereby delays the demixing, because of which the macrovoid formation is avoided [2, 4-6]. Moreover, the mechanical strengths also improve as a result of an increase in the polymer loading [4, 5]. However, increasing the polymer concentration too much can be counterproductive as it can significantly reduce the permeance of the membrane [5-7].

In a TIPS process, where phase inversion is brought about by temperature change, the initial concentration of the dope will decide the region in the binary phase diagram it may end up in, as was shown in Figure 2.8 in section 2.8.1. This would then ultimately decide the membrane morphology [8, 9].

Just like the TIPS, the thermodynamics of a CCD process is also governed by the binary phase diagram (as shown earlier in Figure 2.10 in section 2.11.3) and so the polymer concentration will also play a role in influencing the CCD membrane morphology. For PES based CCD membranes, two different polymer concentrations were investigated 15wt% and 20wt.% and the latter produced membranes with smaller pore sizes and reduced pure water permeance [10]. These results were summarised in Table 2.5 in section 2.12. However, for

PVDF so far only 20wt.% polymer dope solution concentration was used which produced membranes with 30 nm pore sizes and pure water permeance of 570 LMH.bar⁻¹ [11]. A systematic study of varying dope solution concentrations is not undertaken. Therefore, in this chapter, PVDF based CCD membranes were produced by varying the dope solution concentrations between 10-20wt.% and the morphology of the prepared membranes in addition to its basic permeation characteristics studied. For comparison purposes, NIPS based PVDF membranes were also prepared at these varying concentrations to validate the earlier claims of the superior permeation performance of CCD membranes over their NIPS counterparts.

The influence of polymer concentration on CCD membrane morphology is further studied by undertaking a proof of concept study involving a dual-casting approach. In its study on CCD membrane formation mechanism, Wang et al. owe the asymmetric structure of the membrane to the temperature gradient that is developed on account of the unidirectional cooling that is applied to the cast film [10]. The low temperatures facilitate the crystallisation of the solvent molecules, however, the size of crystal growth is determined by the temperature gradient developed in the polymer cast film. The relatively colder end of the cast film produces solvent crystals much smaller in size, compared to the warmer end that has a much larger interconnected crystal structure. Therefore after the leaching of the solvent crystals, the result is an asymmetric membrane where the tight skin separation layer is formed closer to the colder end and the support layer comprising of several interconnected microchannels is formed towards the warmer end. In addition to the temperature gradient, it is also proposed that the concentration of the dope used would also influence the porosity in the separation and support layers of the membranes.

Based on this hypothesis, a proof of concept study is undertaken, which involves casting two layers on top of one another using the same polymer dope but at different concentrations. The aim is to make the support layer more porous to substantially enhance the permeation properties while keeping the rejection properties still intact. And so the top layer which forms the support is cast using a relatively lower polymer concentration dope.

Post fabrication, these dual-cast membranes are characterised for their mean flow pore sizes, pure water permeances and mechanical strengths, and are then compared to their single-cast counterparts.

4.2 Methodology

4.2.1 Materials and Dope preparation

Using the materials mentioned in section 3.1, and PVDF and DMSO were mixed in desired proportions and then placed in an oven overnight at 80°C to obtain a homogenous solution. The homogenous solutions were then used for the casting process to make the membranes.

4.2.2 Membrane Preparation

4.2.2.1 Single-cast membranes

CCD membranes were prepared following the 3-step process described in section 3.2. For NIPS membranes, the dope solution was first cast on a solid support, following which it was immersed in a deionised water bath at room temperature to induce phase separation. The membrane casting thickness was maintained at 0.5 mm for both CCD and NIPS membranes to allow for a fair comparison. Each batch of these single-cast membranes produced by NIPS or CCD, using a particular dope solution concentration is given a sample ID. These are summarised in Table 4.1

A comparative study was then performed for both CCD and NIPS membranes made from these varying concentrations of PVDF dopes.

Table 4.1. Sample IDs of the single-cast membranes with its corresponding dope concentration and preparation method

Sample ID*	PVDF dope conc. (wt.%)	Membrane preparation method
10PVDF_NIPS	10	NIPS
15PVDF_NIPS	15	NIPS
20PVDF_NIPS	20	NIPS
10PVDF_CCD	10	CCD
15PVDF_CCD	15	CCD
20PVDF_CCD	20	CCD

* Sample = "X"PVDF_"Y"

"X" = PVDF dope conc. (wt.%) used

"Y" = Preparation Method

4.2.2.2 Dual-cast membranes

The preparation of dual-cast CCD membranes involved casting two layers of PVDF dope solutions at different concentrations, one on top of the other. The two layers were simultaneously cast using a specially designed, in-house built, two-blade casting knife. The bottom layer, which would determine the separation property, was cast using a high polymer concentration dope to produce a dense separation layer. The top layer, on the other hand, was cast using a lower polymer concentration dope to ensure a higher porosity can be attained in the support. The casting thickness of the bottom layer was kept at 0.05 mm while that of the top layer was kept at 0.45 mm to keep the overall casting thickness of the dual-cast membrane at 0.5mm (which is the same as what was kept for single-cast membranes). The schematic of the dual-cast arrangement is shown in Figure 4.1. The fabrication process then follows the same as that for single-cast CCD membranes (section 3.2). Two types of dual-cast CCD membranes were prepared where the bottom layer dope concentration was fixed at 20wt.% while the top layer concentration varied. The sample ID allotted to the dual-cast CCD membranes along with the dope solution concentrations used for the casting of the two layers are summarised in

Table 4.2.

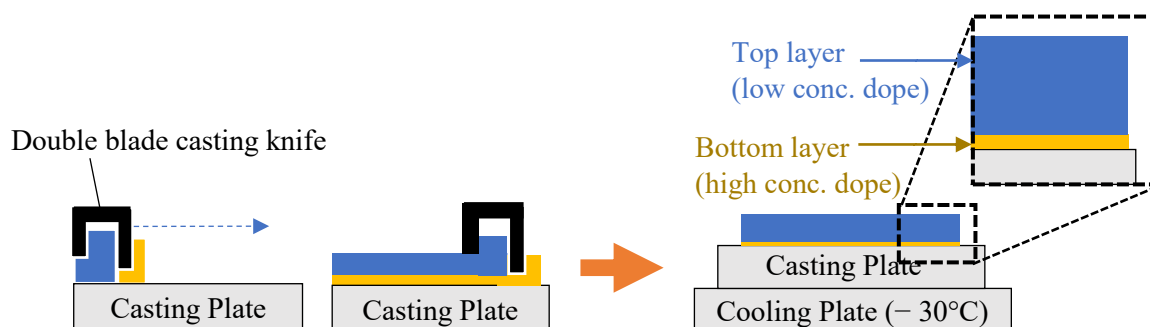


Figure 4.1. Schematic showing the dual-casting arrangement used

Table 4.2. Compositions of the dual-cast CCD membranes

Membrane Sample**	Bottom layer PVDF dope conc. (wt.%)	Top layer PVDF dope conc. (wt.%)
20PVDF_10PVDF_CCD	20	10
20PVDF_15PVDF_CCD	20	15

**Sample = "X"PVDF_ "Y"PVDF_CCD

"X" = PVDF dope conc. (wt.%) used to cast the bottom layer

"Y" = PVDF dope conc. (wt.%) used to cast the top layer

4.2.3 Membrane characterisation

The prepared membranes were studied for their morphology (observed using SEM), permeation characteristics (pore sizes and pure water permeances) and mechanical strengths following the procedure highlighted in section 3.3.

4.3 Results

4.3.1 Scanning Electron Microscopy (SEM)

SEM image results for single-cast 20PVDF_CCD are presented in Figure 4.2-1a to 1d. It shows the typical CCD membrane structure, with a tight skin separation layer (red arrow in Figure 4.2-1a) and a porous support layer (blue arrow in Figure 4.2-1a) having interconnected micro-channels [10, 11]. Comparatively, typical PVDF NIPS membranes have a tight skin in the separation layer along with large finger-like voids extending in the sponge-like support layer [4, 11-14] as seen in Figure 4.3.

The distinguishing features that contribute to a higher permeability for CCD membranes are the high surface pore density and the interconnected and oriented micro-channel structure that considerably reduces the membrane tortuosity (see section 4.3.2). NIPS membranes on the other hand have a very low surface pore density and a large dead pore volume in their support layer [11].

For dual-cast membranes, SEM image results of only 20PVDF_10PVDF_CCD (Figure 4.2-2a to 2d) are presented alongside the single-cast 20PVDF_CCD (Figure 4.2-1a to 1d). This is because the structural differences are more observable in this scenario, because of a higher concentration difference in the two cast layers. The top and bottom layers of the dual casting arrangement shown in Figure 4.1 are seen in a reversed order in the SEM image cross-section of the prepared dual-cast membrane (Figure 4.2). The thin bottom cast layer of Figure 4.1 represents the top separation layer in red in Figure 4.2-2a, while the thicker top cast layer of Figure 4.1 represents the bottom support layer in blue in Figure 4.2-2a.

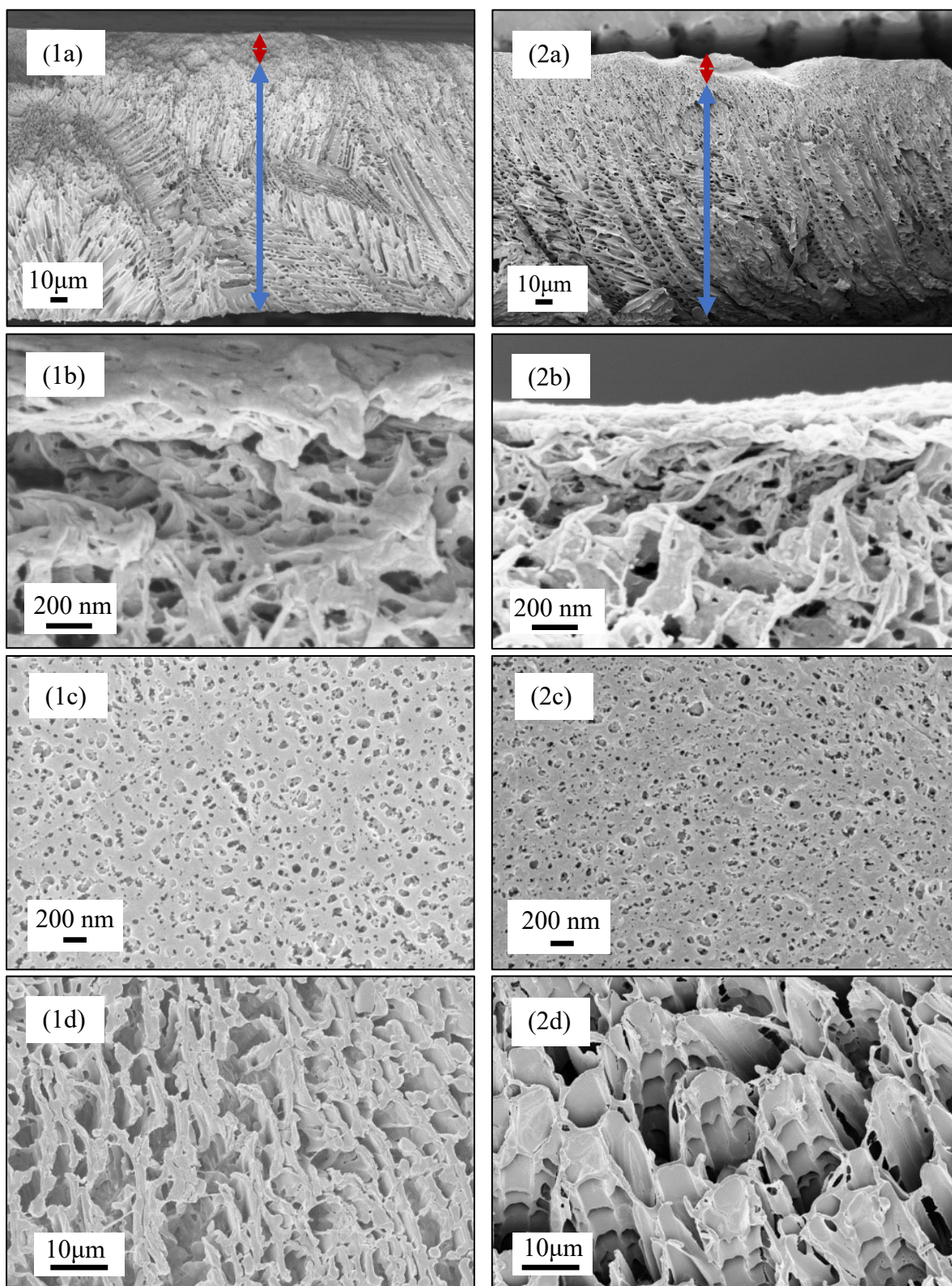


Figure 4.2. SEM images of (a) entire membrane cross section showing the separation layer in red and support layer in blue, (b) higher magnification of the separation layer cross-section, (c) top view and (d) bottom view of (1-left column) single-cast 20PVDF_CCD and (2-right column) dual-cast 20PVDF_10PVDF CCD membrane

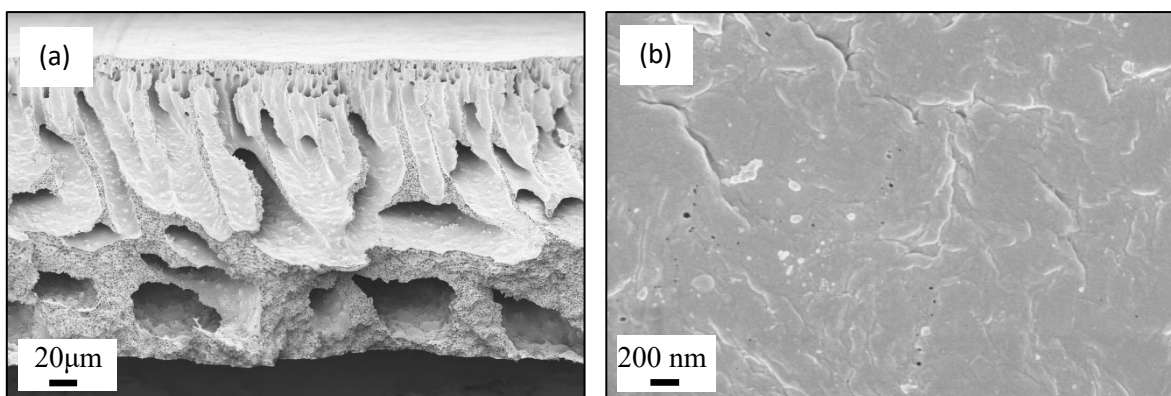


Figure 4.3. SEM image of (a) membrane cross section and (b) separation side surface for 20PVDF_NIPS

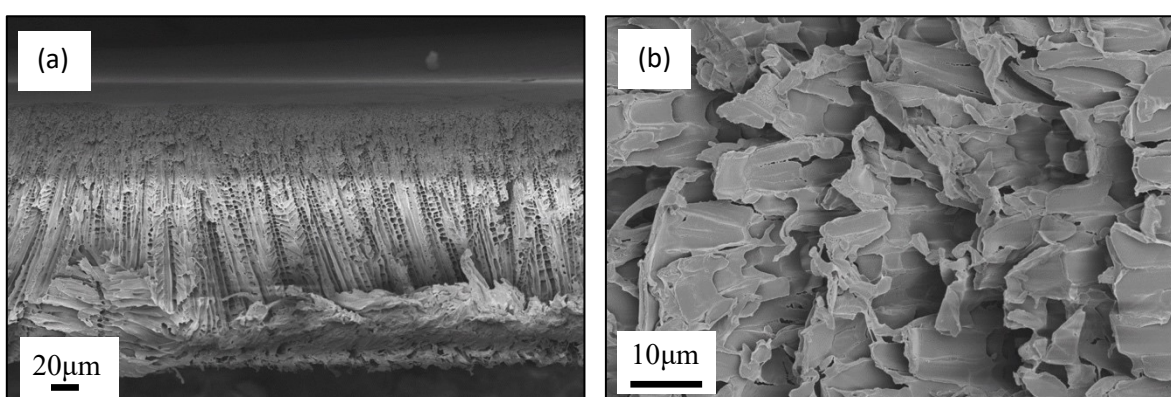


Figure 4.4. SEM image of (a) membrane cross section (b) support side surface for 10PVDF_CCD

The cross-section images (Figure 4.2-1a and 2a) show that the separation layer for both the single-cast and the dual-cast membranes look very similar. Even at higher magnification of the separation layer (Figure 4.2-1b and 2b), both the membranes show a tight dense structure. In fact, the top view images (Figure 4.2-1c and 2c) of the separation surfaces, are almost identical. This is because for both the membranes, the region next to the casting plate had the same polymeric dope concentration at 20wt.%. The difference in the structure of the two membranes lies in its support layers owing to the difference in the polymer concentrations constituting that layer. While the single-cast membrane cross-section was composed of 20wt.% dope solution entirely including its support layer, the dual-cast membrane had its support layer composed of 10wt.% polymer dope. As result, the bottom view images (Figure 4.2-1d and 2d), showing the support surfaces, show that the pores on this surface are much larger for the dual-cast membrane than they are for the single-cast membrane. This suggests that the size of the solvent crystals growing in the support layer would be larger for the former.

Additionally, Figure 4.4 shows the cross-sectional image and the bottom view of the single-cast 10PVDF_CCD membrane. One can tell that the bottom view of the dual-cast 20PVDF_10PVDF_CCD, is now very similar to that of single-cast 10PVDF_CCD. Thus, it can be concluded that for the dual-cast 20PVDF_10PVDF_CCD membrane, the top separation side is very similar to the top separation side of single-cast 20PVDF_CCD, while the bottom support side is very similar to the bottom support side of single-cast 10PVDF_CCD.

Dual-layered membranes have also been prepared in the past using traditional membrane manufacturing methods [15, 16]. They usually use different polymers to cast the two layers to tailor the membrane properties in a certain way. Many times, the two polymers may not be compatible with each other, which can result in instability and delamination between the layers. However, the dual casting technique used in this study uses the same polymeric solution but merely at different concentrations. As a result, the dual-cast CCD membrane still appears as uniform as a single-cast membrane, with no distinct irregularities observed. This in turn eliminates any possibilities for delamination.

Mean flow pore size **Error! Reference source not found.**

Table 4.3. Mean flow pore sizes of both single and dual-cast membranes

Sample	Mean flow pore size (nm) ^{a,b}	
	CCD	NIPS
Single-cast membranes		
10PVDF	47 ± 4	45 ± 2
15PVDF	40 ± 3	36 ± 4
20PVDF	33 ± 2	33 ± 2
Dual-cast membranes		
20PVDF_10PVDF	27 ± 6	N/A
20PVDF_15PVDF	32 ± 1	N/A

^a The uncertainty in the mean flow pore size here represents the sample standard deviation in the mean flow pore sizes obtained from different samples measured. The resolution of the porometer was 2 nm and so although sometimes the measurements may provide a much smaller deviation (<1 nm), the uncertainty in the measurement was taken to be at least half of the resolution which is 1 nm.

^b The deviation does not however represent the full width at half maximum (FWHM) of the pore size distribution.

Table 4.3 summarises the mean flow pore sizes for the various membranes prepared. For the single-cast membranes, as one would expect, an increase in the polymer dope concentration results in a decrease in the mean flow pore size. In fact, for the same polymer concentration dopes, both CCD and NIPS membranes have very similar pore sizes within experimental uncertainties, which imply that both should have similar rejection properties. For the dual-cast CCD membranes, the mean flow pore sizes are very similar to that of single-cast membranes prepared using 20wt.% PVDF dope, which mean that the rejection properties of the two are very similar.

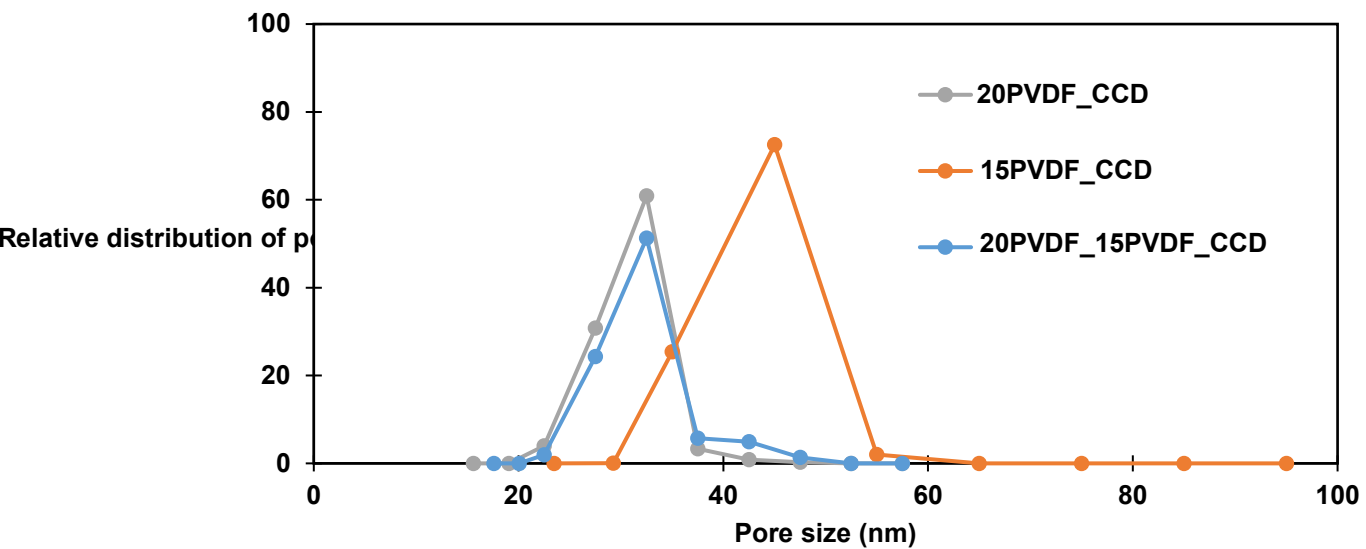


Figure 4.5. Pore size distribution of 20PVDF_CCD, 15PVDF_CCD, and 20PVDF_15PVDF_CCD

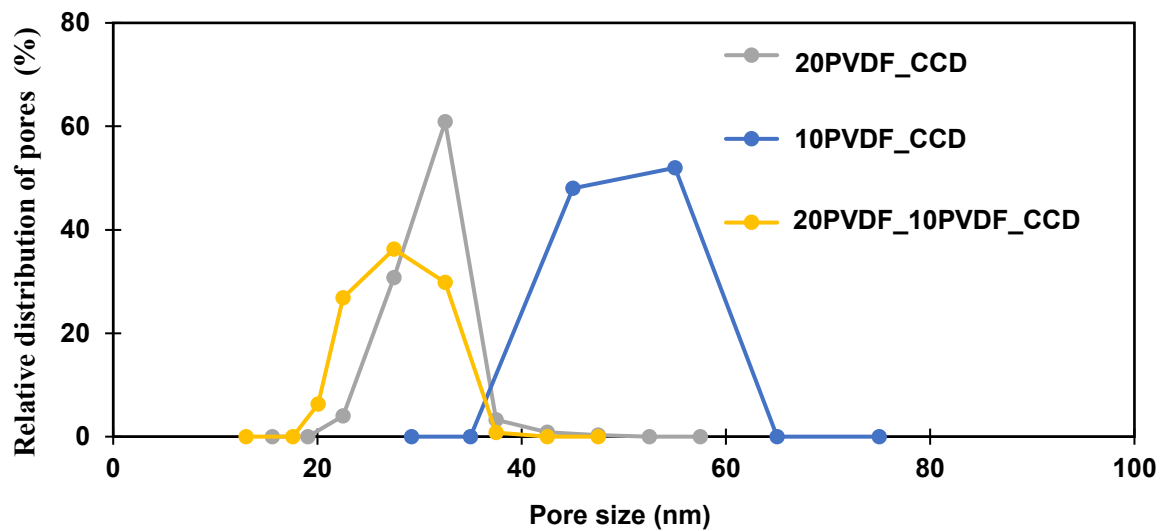


Figure 4.6. Pore size distribution of 20PVDF_CCD, 10PVDF_CCD, and 20PVDF_10PVDF_CCD

Figure 4.5 presents the pore size distribution of single-cast 20PVDF_CCD and 15PVDF_CCD along with that of the dual-cast 20PVDF_15PVDF_CCD. As can be seen the pore size distributions for all three CCD samples are rather narrow. This is in contrast to the NIPS membranes that have much wider pore size distributions [17]. From Figure 4.5, it can be seen that the pore size distribution of dual-cast 20PVDF_15PVDF_CCD is identically similar to that of single-cast 20PVDF_CCD. The distribution of single-cast 15PVDF_CCD on the other hand is more so towards larger pore sizes. Similarly,

Figure 4.6 shows that the pore size distribution of 20PVDF_10PVDF_CCD also very much resembles that of 20PVDF_CCD, while 10PVDF_CCD have much larger pore sizes. This reinforces the fact that the concentration of the dope solution used in the region close to the casing plate can dictate the formation of the separation layer. Thus, one can tailor the rejection properties of the membrane by merely changing the concentration of the dope used in casting the bottom layer. Additionally, it can also be concluded that the concentration of dope used to cast the top layer has little influence on the separation properties of the membrane.

4.3.2 Pure Water Permeance (PWP)

The PWP results for single-cast membranes in Figure 4.7 shows that a decrease in the polymer dope concentration increases the PWP of the membrane. This is expected because a lower polymer concentration gives a membrane higher porosity and enlarged pores, which results in reduced resistance to water permeation flows. On comparing the permeation performance of CCD membranes to their NIPS counterparts, the former wins significantly than the latter in all three scenarios. The difference in permeation performance is substantial given both the membrane types have similar mean flow pore sizes when prepared using the same polymer dope concentration.

In a previous study, where similar cooling and casting conditions were used to make PVDF CCD membranes using 20wt.% concentration dope, the pore sizes and PWP of the prepared membranes were reported to be around 29 nm and 570 LMH.bar⁻¹ respectively [11]. Although the pore size of 20PVDF_CCD prepared in this study remains closely similar, the PWP achieved has more than doubled. This could be due to the optimizing of the cooling process by experience, to ensure a more uniform contact is maintained between the casting and cooling plates. This could lead to an increase in the solvent nucleation sites resulting in a more porous membrane and therefore an enhancement in the permeance.

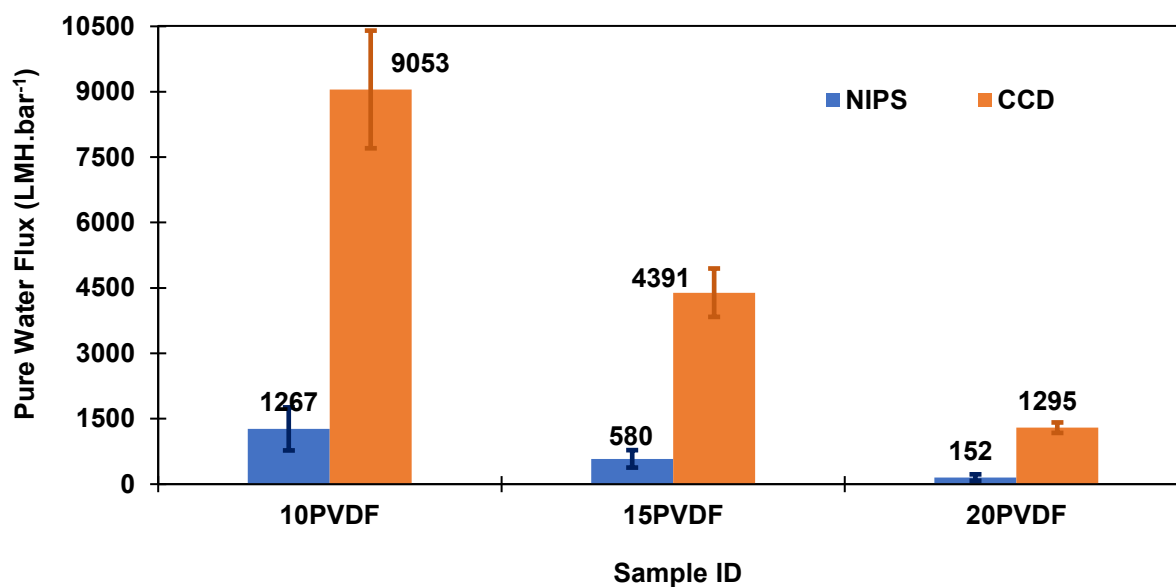


Figure 4.7. PWP results of various single-cast CCD and NIPS membranes

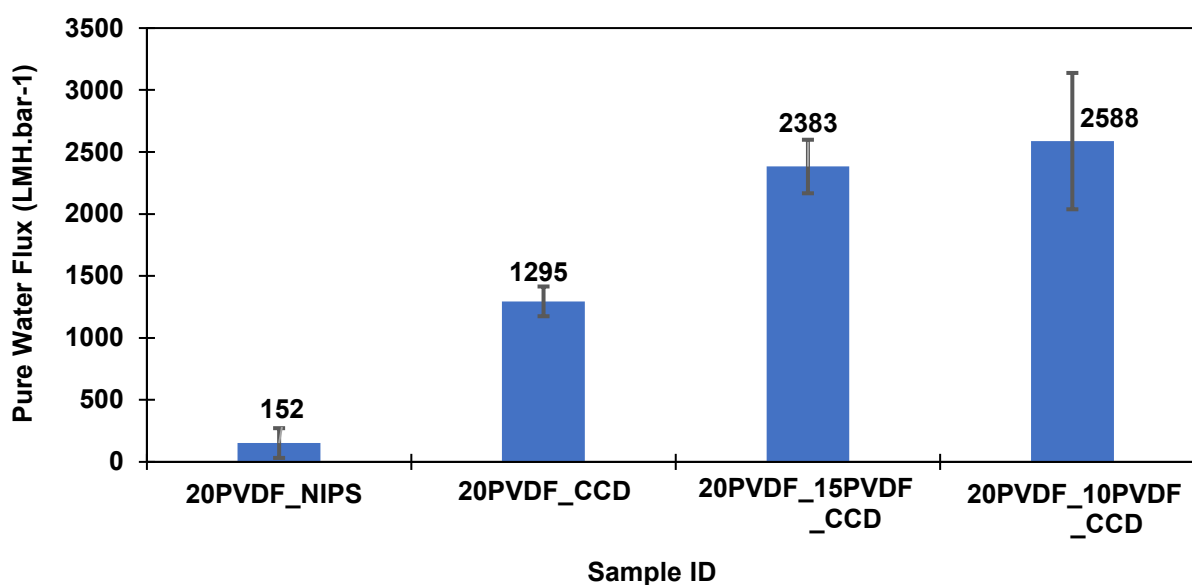


Figure 4.8. PWP results of dual-cast CCD membranes in comparison with their single-cast counterparts

Figure 4.8 then shows the PWP results of the dual-cast CCD membranes alongside the single-cast CCD and NIPS membranes prepared using 20wt.% polymer dope. All four samples, i.e 20PVDF_NIPS, 20PVDF_CCD, 20PVDF_15PVDF_CDD and 20PVDF_10PVDF_CCD, that have almost the same mean flow pore sizes, have a significantly higher PWP for the latter two membranes that are produced via the dual-cast CCD route. While the tightness of the separation layer can be gauged by the mean flow pore size, the role of the support layer in

contributing to the overall membrane transport resistance can be judged by the PWP measurement. The PWP of both the dual-cast CCD membranes is higher by almost 85% when compared to the single-cast CCD counterpart. This shows that in the dual-casting arrangement (Figure 4.1), the lower concentration dope that is used to cast the top thicker layer increases the porosity in the support, which in turn minimizes the overall flow resistance. The improvement in PWP in dual-cast CCD membranes is so high that on comparing them to the 20PVDF_NIPS membrane, the former have permeances that are higher than the latter by almost 15 times. This shows the potential of the dual-casting technique when applied to the CCD method, to obtain superior permeation performance, without compromising the membrane's rejection. On decreasing the concentration of the support layer in the dual-cast membrane from 15wt.% to 10wt.%, there is only a slight improvement in the PWP. This indicates that the resistance contribution of the separation layer, which is very similar in both the dual-cast membranes owing to the same dope concentration (20wt.%) used to cast this layer, now becomes the limiting factor.

It is for the first time that such high PWPs ($2300\text{--}2600\text{ LMH}\cdot\text{bar}^{-1}$) have been achieved for pure PVDF membranes in the ultrafiltration range with pore sizes around 30 nm. Table 2.2 in section 2.10.1 presented PWPs of UF PVDF membrane produced by other researchers using the NIPS process. It showed the PWP for pure PVDF membranes to be around $150\text{ LMH}\cdot\text{bar}^{-1}$, similar to our in-house PVDF-NIPS membranes. The same was true for industry standard commercial PVDF membranes that also showed similar permeances (Table 2.3 in section 2.10.2). Graft copolymers such as PVDF-g-PEGMA that enhanced the permeation properties of PVDF-NIPS membranes significantly [18-21], could also be used for these dual-cast PVDF-CCD membranes to push the limits of achievable permeances even further. But this method does demand additional chemical synthesis and processing and also results in weak mechanical properties and wide pore size distributions in its membranes [18, 21-23]. Hence, it may not be ideal for scalable commercial production.

4.3.3 Mechanical strength

The tensile strengths of both single and dual-cast CCD membranes were investigated to gauge the differences in their mechanical properties. The result is presented in Table 4.4. It can clearly be seen that for the single-cast membranes as the polymer dope concentration decreases the maximum load withstanding capacity and the tensile stress also decreases. Although the strain factor at maximum load is only slightly higher for 20PVDF_CCD

compared to 10PVDF_CCD and 15PVDF_CCD, the Young's modulus (=stress/strain), which indicates the resistance of the membranes to undergo deformation under stress, is significantly higher for 20PVDF_CCD compared to its lower concentration counterparts. This would be expected because given the same membrane thickness, the membranes prepared with a lower polymer concentration have a lower mass per unit area, and hence a reduced capacity to withhold the load. As a result, the mechanical properties of the membrane deteriorate with a reduction in the polymer concentration.

The dual-cast CCD membranes have mechanical properties similar to those of the single-cast 10PVDF_CCD and 15PVDF_CCD samples respectively. This is because the majority (90%) of the membrane composition of a dual-cast membrane is composed of the lower polymer dope concentration. Thus, although the PWP of 20PVDF_10PVDF_CCD was marginally higher than that of 20PVDF_15PVDF_CCD, there is a significant deterioration in the mechanical properties of the former compared to the latter. Hence, 20PVDF_15PVDF_CCD would be a better choice overall compared to its other dual-cast counterpart.

Table 4.4. Tensile test results of both single and dual-cast CCD membranes

Sample	Thickness (mm)	Tensile Stress (MPa)	Maximum Load (N)	Elongation at max. load (%)	Young's modulus (MPa)
10PVDF_CCD	0.19 ± 0.01	0.9 ± 0.1	2.0 ± 0.3	29 ± 04	24 ± 03
15PVDF_CCD	0.20 ± 0.02	1.6 ± 0.1	3.2 ± 0.4	36 ± 04	49 ± 7
20PVDF_CCD	0.19 ± 0.01	2.7 ± 0.2	4.8 ± 0.5	41 ± 16	107 ± 16
20PVDF_10PVDF_CCD	0.23 ± 0.02	1.1 ± 0.1	2.5 ± 0.3	33 ± 10	31 ± 03
20PVDF_15PVDF_CCD	0.20 ± 0.01	1.7 ± 0.2	3.4 ± 0.6	44 ± 12	51 ± 05

The PWP of 20PVDF_15PVDF_CCD was also tested for a longer duration of three hours and no reduction in permeance as a result of membrane compression was observed. This is owed to the characteristic CCD membrane cross-section morphology. CCD membranes have oriented microchannels that increase in size from the separation layer to the support side and have PVDF grains that are tightly connected in between their walls [11]. Moreover, PVDF-

CCD membranes are composed predominantly of β -phase and γ -phase PVDF crystals, which give them a higher level of compression resistance [11].

PVDF-NIPS membranes on the other hand have large finger-like voids and are composed mainly of the α -phase PVDF [11]. In a previous study, which compared the mechanical properties of PVDF CCD membranes with those of PVDF NIPS membranes, showed that the former had much better resistance to high compression pressures than the latter [11]. The membranes were subjected to high pressure of 34.5 bar, where the CCD membrane retained its original morphology along with the overall membrane thickness while the NIPS membrane was severely compressed with a reduction in membrane thickness by almost 75%.

4.4 Discussion

The enhanced permeation performance of single-cast PVDF CCD membranes relative to their NIPS counterparts can be attributed to the characteristic asymmetric structure of CCD membranes as seen in the SEM images in Figure 4.2. During the CCD fabrication process, when the casting plate is placed in contact with the cooling plate, rapid heat dissipation occurs from one end of the casting plate. The polymer cast layer itself, however, is a poor conductor of heat, which results in a temperature gradient being established in the cast layer. The low temperatures facilitate the crystallisation of solvent molecules throughout the cast layer, but the extent of crystal growth, as described by Wang et al.[10], is dependent on the temperature and polymer concentration and gradients that are developed.

The growth of crystals can be described in three phases as illustrated in Figure 4.9. In phase 1, solvent molecules nucleate heterogeneously from the metal plate surface and form polymer-free solvent frozen front covering the surface of the plate. As a result, the polymer molecules are ejected out and form a thin layer of high polymer concentration locally next to this frozen front, resulting in a concentration gradient being established.

Phase 2 of crystal growth is in the thin region next to the frozen front, where the temperatures are still low. Here homogeneous nucleation of solvent molecules takes place and the size of these solvent crystals increase moving away from the frozen front, owing to both thermodynamic and kinetic factors. From a thermodynamic standpoint, a lower temperature and a higher polymer concentration favours phase separation through gelation, which limits the time for crystal growth. From the kinetic standpoint too, a high polymer concentration and low temperature results in a retardation of the polymer-solvent diffusion rates which limits their

exchange at the solvent crystal interface. Thus, in regions close to the casting plate where the polymer concentration is the highest and the temperature the lowest, the size of solvent crystals homogeneously nucleated is the smallest. These solvent nuclei developed in phase 2 eventually grow and end up connecting together, given the high volume fraction of the solvent that is present.

In the warmer end spectrum of the cast film, there isn't sufficient activation energy to allow for homogenous nucleation of the solvent crystals. Therefore, the solvents homogeneously nucleated in phase 2, continue to grow in this region in an oriented manner to form interconnected cellular structures (phase 3).

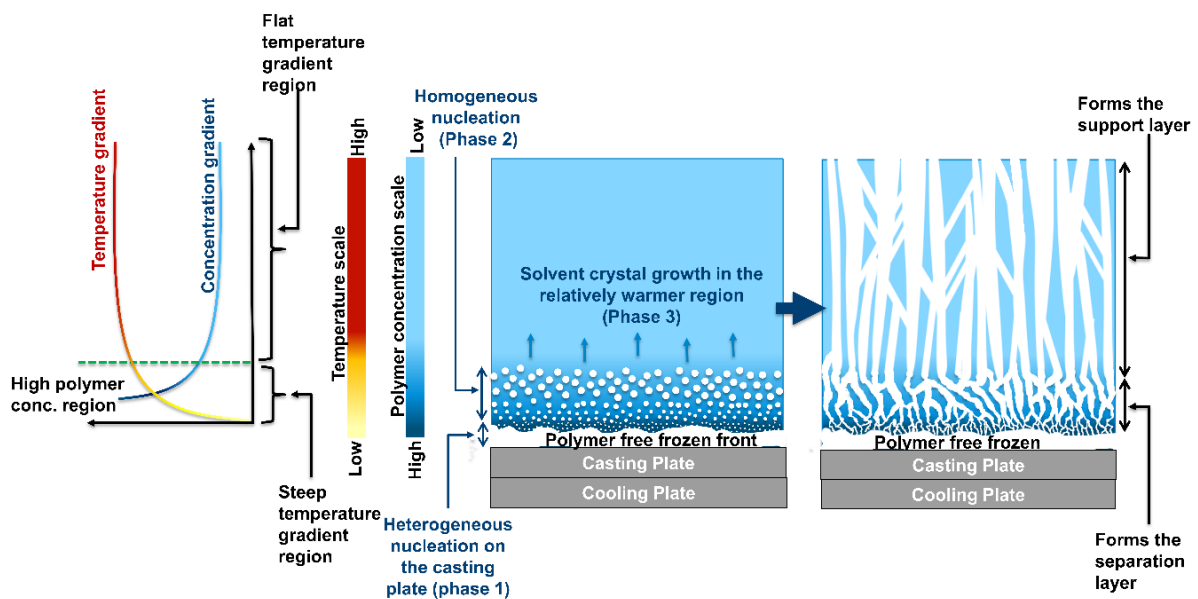


Figure 4.9. Illustration of crystal growth mechanism involved in CCD

After the leaching of the solvent crystals, the result is an asymmetric membrane, having a tight skin-like separation layer (the relatively cooler region of the cast layer-1st and 2nd phase) and a support layer that is characterised by a porous interconnected microchannel structure (the relatively warmer region-3rd phase). It is this structure that is responsible for high permeation performance in CCD membranes while keeping the rejections still intact.

The dual-casting technique tries to exploit the characteristic asymmetric structure of CCD membranes even further by using a relatively lower polymer concentration dope to cast the top thicker layer which eventually influences the support layer. The aim was to make this support layer more porous and have less transport resistance. The lower polymer concentration results in both a longer time for the solution surrounding the crystal to undergo gelation as well

as enhances the polymer-solvent diffusion rates at the interface. This, therefore, results in the formation of larger diametrical cellular structures. This is particularly evident when one compares the cross-section and support side surface SEM images of dual-cast 20PVDF_10PVDF_CCD membrane (Figure 4.2- 2a and 2d) to that of single-cast 20PVDF_CCD membrane (Figure 4.2-1a and 1d). The former has a more porous support layer and larger support side pore sizes than the latter. Even the PWP results which show a significant enhancement in the permeation performance of dual-cast CCD membranes suggest that the porosity has indeed increased.

The bottom thinner layer, one in contact with the casting plate, which influences the separation property, is also polymer concentration dependent. Using the same polymer dope concentration in the region next to the casting plate, for both dual and single-cast CCD membranes, results in practically the same solvent-crystal structure in this region for both the membrane types. Both the mean flow pore size (Table 4.3) and separation side surface images (Figure 4.2- 1c and 2c) are therefore identically similar, which suggest them both having very similar rejection properties.

This, therefore, illustrates the possibility of influencing either the support or separation layer individually, by merely changing the dope composition of that layer.

The tensile stress test results give an insight into practical implications that need to be considered when applying the dual-casting technique. It suggests that decreasing the concentration of the top layer, which constitutes almost 90% of the membrane casting thickness, may have implications on the mechanical robustness of the membranes. This was evident in the case of 20PVDF_10PVDF_CCD and 20PVDF_15PVDF dual-cast CCD membranes, where although there was a marginal improvement in the permeability of the former compared to the latter, the mechanical properties were severely compromised in the former. Therefore, whenever dual-casting technique is applied, an optimum concentration should be used to cast the top layer such that the enhancement in permeation properties is not at a significant cost in terms of the mechanical robustness of the membranes. An alternative to increasing the permeance even further but not compromising the mechanical properties of the membrane substantially, would be to try and decrease the thickness of the separation layer while increasing the thickness of the support layer. This can be something for further investigation to see the effect of changing the casting layers' thicknesses while keeping the polymer dopes constituting these layers unchanged.

4.5 Conclusion

This chapter investigated the effect polymer dope concentration has on the morphology and performance of PVDF membranes made by the CCD method. It was concluded that the polymer dope concentration influences the extent of solvent crystal growth which then ultimately decides the pore sizes and permeability of the prepared membranes. The PVDF NIPS membranes that were prepared for comparison purposes showed similar rejections but considerably poorer permeances.

The new dual-casting approach was implemented on the CCD membranes to further exploit the effect of different dope concentrations on the membrane morphology. The results showed a significant improvement in PWP in dual-cast CCD membranes compared to the single-cast ones, while still maintaining the mean flow pore size. For instance, a dual-cast CCD membrane had a PWP which was higher by 85% than its single-cast CCD counterpart and higher by 15 times than its single-cast NIPS counterpart. The mean flow pore sizes remained similar, around 33nm, for all three membrane types. This suggested that the increase in the permeance was not at the cost of the membrane's rejection capabilities but more as the consequence of an increase in the porosity of its sublayer. This was evident from the SEM image results. The mechanical stress test results highlighted the importance of choosing an optimum polymer concentration dope to cast the two layers such that an improvement in permeance is not at the expense of a significant deterioration in the mechanical properties of the membrane. The successful implementation of the dual-casting technique also reaffirmed the hypothesis of the crystal growth mechanism involved in the CCD method.

This major breakthrough in permeation performance achieved through the application of the dual-casting technique to the CCD method, will consequently reduce the total membrane area required for any given filtration process and significantly bring down the capital and operating expenses. This would in turn lead to an improvement in the economic viability of membrane-based water treatment systems and therefore result in its wider acceptance and application in several parts of the globe.

4.6 References

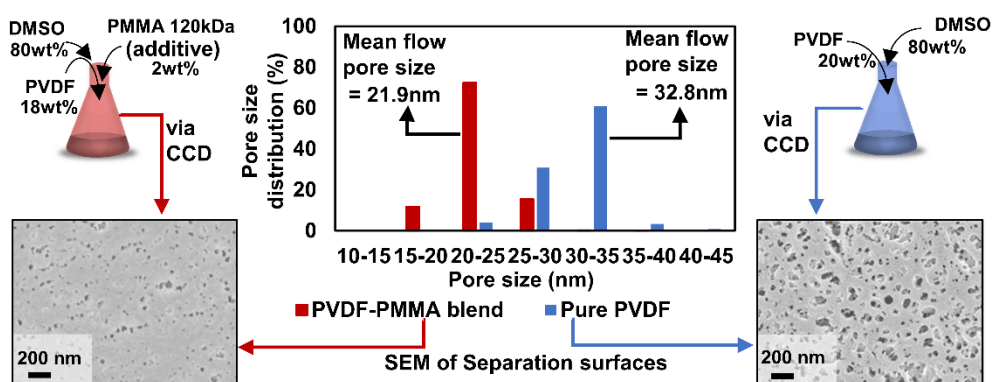
1. Smolders, C.A., et al., *Microstructures in phase-inversion membranes. Part 1. Formation of macrovoids*. Journal of Membrane Science, 1992. **73**(2): p. 259-275.
2. Holda, A.K. and I.F.J.J.o.A.P.S. Vankelecom, *Understanding and guiding the phase inversion process for synthesis of solvent resistant nanofiltration membranes*. 2015. **132**(27).
3. Simone, S., *Coagulation Bath*, in *Encyclopedia of Membranes*, E. Drioli and L. Giorno, Editors. 2015, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 1-2.
4. Jung, J.T., et al., *Understanding the non-solvent induced phase separation (NIPS) effect during the fabrication of microporous PVDF membranes via thermally induced phase separation (TIPS)*. Journal of Membrane Science, 2016. **514**: p. 250-263.
5. Kahrs, C., T. Gühlstorf, and J. Schwellenbach, *Influences of different preparation variables on polymeric membrane formation via nonsolvent induced phase separation*. Journal of Applied Polymer Science, 2020. **137**(28): p. 48852.
6. Holda, A.K., et al., *Study of polymer concentration and evaporation time as phase inversion parameters for polysulfone-based SRNF membranes*. 2013. **442**: p. 196-205.
7. Vandezande, P., et al., *High throughput study of phase inversion parameters for polyimide-based SRNF membranes*. 2009. **330**(1-2): p. 307-318.
8. Matsuyama, H., S. Berghmans, and D.R. Lloyd, *Formation of hydrophilic microporous membranes via thermally induced phase separation*. Journal of Membrane Science, 1998. **142**(2): p. 213-224.
9. Lin, Y., et al., *Formation of a bicontinuous structure membrane of polyvinylidene fluoride in diphenyl carbonate diluent via thermally induced phase separation*. Journal of Applied Polymer Science, 2009. **114**(3): p. 1523-1528.
10. Wang, B., et al., *Porous membranes prepared by a combined crystallisation and diffusion (CCD) method: Study on formation mechanisms*. Journal of Membrane Science, 2018. **548**: p. 136-148.
11. Wang, B., J. Ji, and K. Li, *Crystal nuclei templated nanostructured membranes prepared by solvent crystallization and polymer migration*. Nat Commun, 2016. **7**: p. 12804.
12. Deshmukh, S.P. and K. Li, *Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fibre membranes*. Journal of Membrane Science, 1998. **150**(1): p. 75-85.

13. Bottino, A., et al., *The formation of microporous polyvinylidene difluoride membranes by phase separation*. Journal of Membrane Science, 1991. **57**(1): p. 1-20.
14. Yeow, M.L., Y.T. Liu, and K. Li, *Morphological study of poly(vinylidene fluoride) asymmetric membranes: Effects of the solvent, additive, and dope temperature*. Journal of Applied Polymer Science, 2004. **92**(3): p. 1782-1789.
15. Setiawan, L., et al., *Explorations of delamination and irregular structure in poly(amide-imide)-polyethersulfone dual layer hollow fiber membranes*. Journal of Membrane Science, 2012. **423-424**: p. 73-84.
16. Xia, Q.-C., et al., *A hydrophilicity gradient control mechanism for fabricating delamination-free dual-layer membranes*. Journal of Membrane Science, 2017. **539**: p. 392-402.
17. Kang, G.-d. and Y.-m. Cao, *Application and modification of poly(vinylidene fluoride) (PVDF) membranes – A review*. Journal of Membrane Science, 2014. **463**: p. 145-165.
18. Liu, B., et al., *High performance ultrafiltration membrane composed of PVDF blended with its derivative copolymer PVDF-g-PEGMA*. Journal of Membrane Science, 2013. **445**: p. 66-75.
19. Wang, S., et al., *PVDF ultrafiltration membranes of controlled performance via blending PVDF-g-PEGMA copolymer synthesized under different reaction times*. Frontiers of Environmental Science & Engineering, 2017. **12**(2): p. 3.
20. Wu, Q., et al., *Improving the Performance of PVDF/PVDF-g-PEGMA Ultrafiltration Membranes by Partial Solvent Substitution with Green Solvent Dimethyl Sulfoxide during Fabrication*. ACS Omega, 2019. **4**(22): p. 19799-19807.
21. Loh, C.H. and R. Wang, *Effects of Additives and Coagulant Temperature on Fabrication of High Performance PVDF/Pluronic F127 Blend Hollow Fiber Membranes via Nonsolvent Induced Phase Separation*. Chinese Journal of Chemical Engineering, 2012. **20**(1): p. 71-79.
22. Abed, M.M., et al., *Economical production of PVDF-g-POEM for use as a blend in preparation of PVDF based hydrophilic hollow fibre membranes*. Separation and Purification Technology, 2013. **106**: p. 47-55.
23. Wang, S., et al., *Non-woven PET fabric reinforced and enhanced the performance of ultrafiltration membranes composed of PVDF blended with PVDF-g-PEGMA for industrial applications*. Applied Surface Science, 2018. **435**: p. 1072-1079.

5 Pore size reduction of PVDF-CCD membranes using a blending modification approach

Abstract

So far the smallest pore size achieved for PVDF membranes prepared by the CCD method is about 30 nm. To reduce the pore sizes further would require either increasing the total polymer concentration further or reducing the cooling temperatures lower. Both of these may be undesirable from a large-scale production standpoint. So without changing any operating conditions, this study proposes to use PMMA as a blending additive to the PVDF-DMSO dope to make CCD membranes with reduced pore sizes. A systemic study showed that the pore size reduces when increasing the PMMA concentration in the membranes; but after an initial drop compared to the pure PVDF membrane, the pure water permeance doesn't decline with PMMA concentration. The effect of different molecular weights of PMMA (120kDa and 35kDa) was also investigated, where the results showed a smaller pore size for membranes prepared using a higher molecular weight PMMA. Scanning electron microscopy (SEM), cloud-point temperature measurement and Fourier transform infrared spectroscopy (FTIR) were used to characterise the membranes and help understand how PMMA affects membrane formation. From the evidence gathered, we attribute the effects of PMMA to the change in the number of nucleation centres, diffusional rates, as well as gelation point based on a previously proposed CCD mechanism.



Keywords: PVDF membrane, PMMA, Blend, Pore size, Ultrafiltration, FTIR

5.1 Introduction

The overall objective of this thesis is to develop high-performance membranes suitable for drinking water production. Since most viruses are larger than 20 nm, the aim is to be able to produce membranes that can filter out these viruses by size exclusion and also be better than their commercial counterparts when it comes to the overall permeation performance [1].

While the previous chapter showcased the potential of PVDF CCD membranes in achieving high pure water permeances (PWPs) compared to its NIPS counterparts, the focus of this chapter would be to find an effective way to manipulate the pore sizes of the CCD membranes such that they are below 20 nm. The smallest pore size that was achieved so far for CCD membranes was 33nm. This was produced by increasing the polymer dope concentration to 20wt.% and maintaining the cooling conditions that favour the formation of small pore sizes. The cooling temperature was maintained at -30°C and the cooling rate was kept the fastest by using Aluminium-Aluminium as the cooling-casting plate combination.

To decrease the pore size further, one could either apply an even faster cooling rate or further increase the dope concentration or both. For faster cooling rates, one could either improve heat conduction or use a lower temperature, but these have design challenges or intensified energy requirements associated with them. Increasing the polymer dope concentration further is also challenging as dissolution would be a lot slower, and a higher dissolution temperature might be needed, both of which are undesirable from a production standpoint. Additionally, the PWP would be considerably be affected in membranes prepared with higher concentration dopes owing to the reduced membrane porosity.

This chapter focuses on reducing the pore size of the membranes by neither changing the cooling rates, nor by increasing the polymer dope concentration, but rather by using an additive to the dope solution, namely poly(methyl methacrylate) (PMMA). PMMA was chosen as the additive as it is one of the few polymers that is thermodynamically compatible with PVDF over a wide range of blend compositions. It is also water-insoluble and hydrophilic [2-4]. Alternatively, polyethylene glycol (PEG) which is also compatible could also be chosen; however, PMMA, unlike PEG, is not water-soluble and hence would not get washed away during operation and therefore maintain the membrane porosity [5]. We will show that PMMA can change the thermodynamic and kinetic properties of the polymer solution during the CCD process, and limit solvent crystal growth, resulting in smaller solvent crystals and therefore smaller pore sizes in the final membrane [6].

5.2 Experimental Materials and Method

5.2.1 Materials and Membrane Preparation

In addition to materials mentioned in section 3.1, PMMA of two different molecular weights (120kDa, 35kDa) were used, where 120kDa PMMA was obtained from Merck Sigma Aldrich while 35kDa PMMA was obtained from VWR, UK. Different proportions of PMMA and PVDF were dissolved in DMSO, whilst maintaining the total polymer concentration at 20wt.%, after which the dope solution mixture was placed in an oven overnight at 80°C to obtain a homogenous solution. 25wt.% pure PVDF dope was also used to make CCD membranes, to study the impact of increasing the total polymer dope concentration on the permeation characteristics. The different sample IDs with their dope compositions and the MW of PMMA used are summarised in Table 5.1 [6]. CCD membranes were then prepared following the 3-step process described in section 3.2.

Table 5.1. Sample IDs and their dope compositions (from [6])

Sample ID	PMMA MW (kDa)	PMMA conc. (wt.%)	PVDF conc. (wt.%)	Total polymer conc. (wt.%)
20PVDF-0PMMA	N/A	0	20	20
19PVDF-1PMMA-120kDa	120	1	19	20
18PVDF-2PMMA-120kDa		2	18	20
16PVDF-4PMMA-120kDa		4	16	20
19PVDF-1PMMA-35kDa	35	1	19	20
18PVDF-2PMMA-35kDa		2	18	20
16PVDF-4PMMA-35kDa		4	16	20
25PVDF-0PMMA	N/A	0	25	25

5.2.2 Membrane Characterisation

The prepared membranes were studied for their morphology (observed using SEM), permeation characteristics (pore sizes and pure water permeances) and mechanical strengths following the procedure highlighted in section 3.3.

The relative proportion of PVDF to PMMA in the separation and support surfaces of the membrane was analysed using ATR-FTIR. The details of the analytical equipment can be

found in section 3.3. The samples analysed were raw PMMA (both 35kDa and 120kDa) and PVDF powders used in dope solution preparation, along with the support and surface sides of 20PVDF-0PMMA, 18PVDF-2PMMA-35kDa and 18PVDF-2PMMA-120kDa membranes. For the membranes, to analyse the separation and support surfaces, two smaller samples (0.5cm x0.5cm) were cut next to each other, to try and make sure that the two compared surfaces were from the same position of the membrane, and then the corresponding side was placed facing the diamond crystal of the FTIR spectrometer for analysis.

In addition to these characterisation techniques, cloud point temperatures for dope solutions of various samples were also estimated. For this, the solutions were sealed in glass vials and placed in a temperature-controlled oven. The temperature was initially set at 80°C and subsequently reduced in intervals of 3°C, each lasting 24 hours. At each temperature interval, the solutions of all samples were checked visually to see if the clear solution had turned cloudy.

5.3 Results

5.3.1 SEM

Figure 5.1 shows the membrane morphology of pure PVDF (20PVDF-0PMMA) and PVDF-PMMA blend membranes (18PVDF-2PMMA-120kDa and 18PVDF-2PMMA-35kDa) [6]. The separation side surface images of 20PVDF-0PMMA and 18PVDF-2PMMA-35kDa look very similar, while that of 18PVDF-2PMMA-120kDa shows a much smaller pore size. For support side surface images, the differences between pure PVDF membrane sample (Figure 5.1-1b) and the blend membranes' samples (Figure 5.1-2b and 1-3b) are more distinct, with the pore sizes being much larger on the support side of the pure PVDF membrane compared to the blended ones. The micro-channels characteristic of CCD membranes are clearly seen in the support layer (blue arrow) of 20PVDF-0PMMA cross-section (Figure 5.1-1c), but these are hardly visible in the blend membranes' cross-sections (Figure 5.1-2c and 1-3c). Higher magnification images of the cross-section of the support layer show that the micro-channels do however exist for even the blended ones (Figure 5.1-2d and 1-3d), although they are much smaller in sizes compared to the pure PVDF sample (Figure 5.1-1d). Between the two blended samples, the cross-section images show larger micro-channels in the sample blended with 35kDa PMMA (Figure 5.1-2d) compared to the one blended with 120kDa (Figure 5.1-3d).

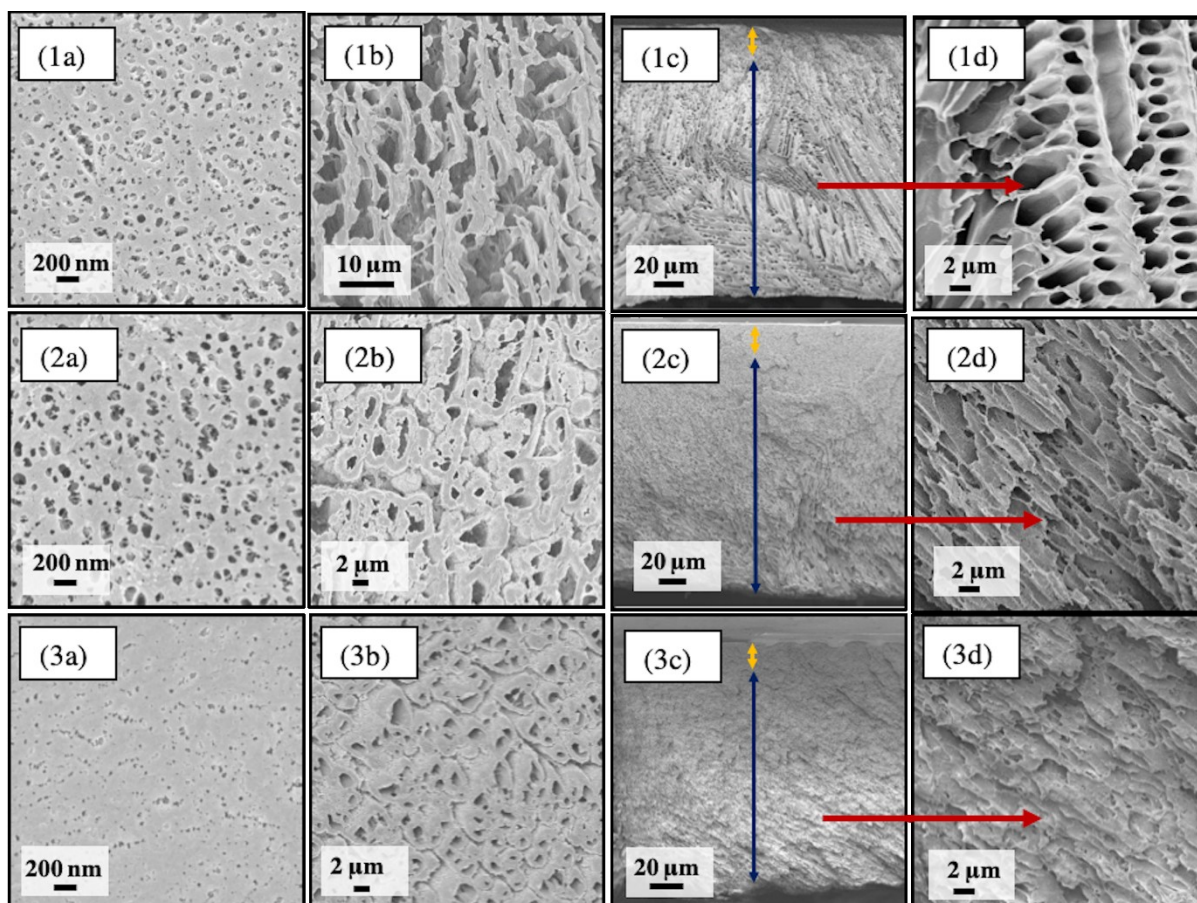


Figure 5.1. SEM images for (1) 20PVDF-0PMMA, (2) 18PVDF-2PMMA-35kDa and (3) 18PVDF-2PMMA-120kDa, showing the (a) separation side surface, (b) support side surface, (c) cross-section with the separation layer (yellow arrow) in the top and support layer (blue arrow) in the bottom, and (d) magnified cross-section of the support layer (from [6])

5.3.2 Mean flow pore size

The mean flow pore size results obtained using liquid-liquid displacement porometry (LLDP) are presented in Figure 5.2 [6]. It clearly shows that increasing the concentration of PMMA from 0% to 4% reduces the mean flow pore size, while still maintaining the total polymer concentration at 20wt.%. On comparing the two blend membranes, for the same dope composition, the one prepared with higher molecular weight PMMA (120kDa) has a smaller pore size compared to the one prepared with the lower molecular weight PMMA (35kDa). In fact, the difference in pore sizes between the two blended membranes increases with an increasing concentration of PMMA.

The reduction in pore size with the addition of PMMA, and this reduction being more prominent for 120kDa PMMA than for 35kDa PMMA, was also witnessed in the SEM images

of the support side surfaces and the magnified cross-sections of the support layer. The SEM images of the separation side surface however, show pore sizes relatively larger than that measured by LLDP. This is because CCD membranes, unlike NIPS membranes, may have their narrowest pore neck region not on the surface but underneath it, owing to the solvent crystal formation mechanism behind CCD as suggested by Wang et al. [7]. As a result, the separation surface SEM images fail to capture this narrowest pore neck region. Moreover, SEM image analysis would not distinguish between dead-end pores and open pores and therefore lead to overestimation of the pore coverage. LLDP on the other hand, only considers the open pore channels that contribute to flow and measures the most constricted region of a channel as its pore diameter. Therefore, for quantitative pore size analysis, LLDP is more suitable while SEM images help understand the membrane morphology. Figure 5.8 illustrates this pore neck region of the CCD membranes.

For 25PVDF-0PMMA, the membrane pore sizes also reduces down below 20 nm. This result is in line with the effect seen in the previous chapter, where the pore sizes reduced down from 47nm to 33 nm by increasing the total polymer dope concentration from 10 to 20wt.% respectively.

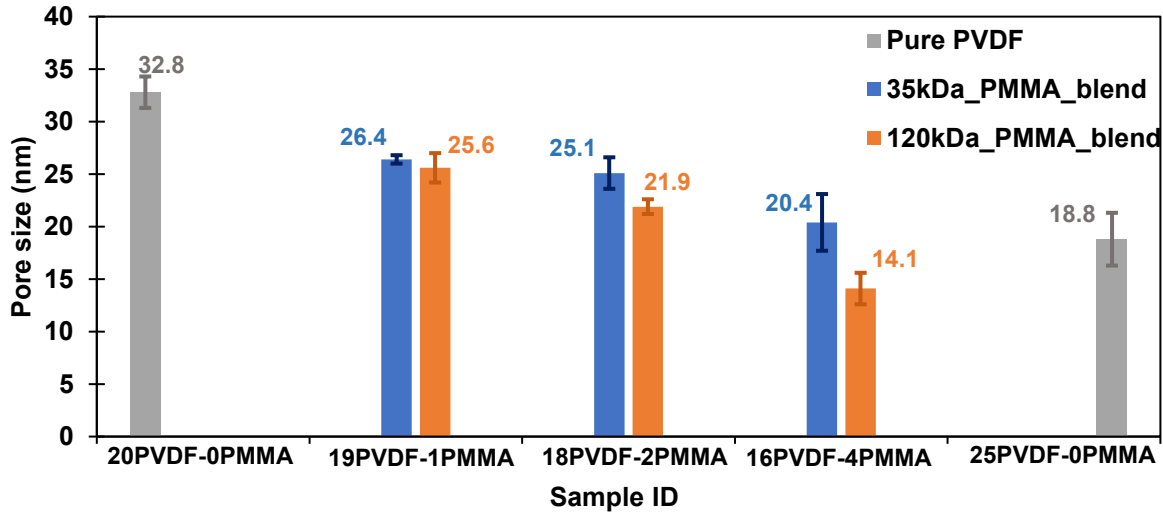


Figure 5.2. Mean flow pore sizes for all samples tested via LLDP (from [6])

5.3.3 Pure water permeance (PWP) and membrane porosity

Figure 5.3 shows the PWPs for the samples under study [6]. The PMMA blended samples, in general, have a lower PWP than the 20PVDF-0PMMA sample. This was expected as PMMA blended samples produced membranes with tighter separation layers and smaller

microchannels, resulting in smaller mean flow pore sizes. Similarly, between the two blended samples, the one prepared with higher molecular weight PMMA (120kDa) shows a poorer PWP in comparison, just as its membranes showed relatively smaller pore sizes.

25PVDF-0PMMA shows an even higher decline in permeance. This shows that simply increasing the polymer dope concentration to reduce the pore size is not an effective way as the PWP of the membrane suffers considerably. 16PVDF-4PMMA-35kDa sample has pore sizes similar to that of 25PVDF-0PMMA, but the PWP is almost 3.4 times higher in the former than it is in the latter.

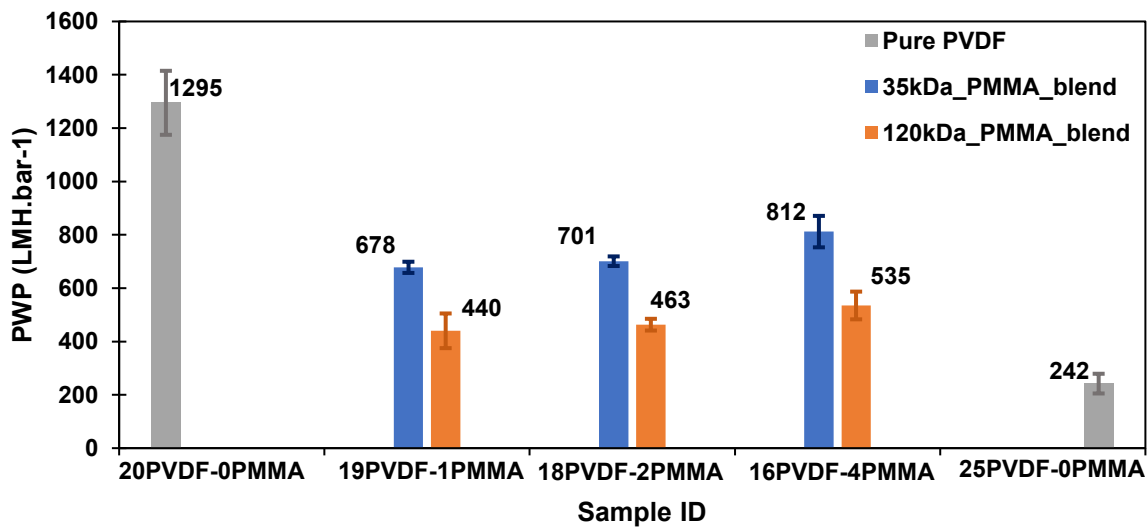


Figure 5.3. Pure water permeances (PWPs) for all samples tested (from [6])

For the blend samples, after an initial drop in the PWP as seen for 19PVDF-1PMMA samples, with increasing PMMA content, the PWP is either maintained or slightly growing. This is particularly surprising as with increasing PMMA content, the mean flow pore sizes decrease, which should also lead to a reduction in PWP but instead, we see an opposite trend. This can be explained by the through-pore membrane porosity presented in Figure 5.4 [6]. These are calculated using Hagen-Poiseuille equation as elaborated in section 3.3.2 and assumes that the pores are cylindrical in shape. The porosity results are very much in line with the permeance results, where they do not decrease with increasing PMMA loading. The membrane porosity calculated here does not include the dead pores but only those that are open to let flow pass through them and so is a more appropriate representation of membrane porosity than that obtained via other methods such as evaporimetry [8].

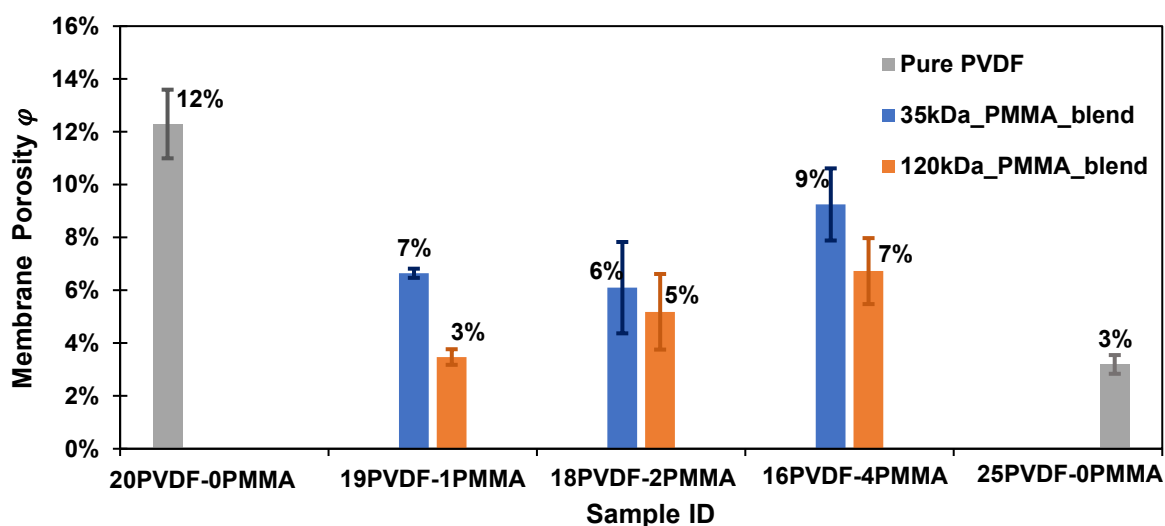


Figure 5.4. Membrane porosity for all samples tested (from [6])

5.3.4 Cloud point temperatures (CPT)

The cloud point temperature (CPT) for each sample is presented in Table 5.2 [6]. CPT was determined by observing the temperature at which the clear solution turns cloudy, as illustrated in Figure 5.5 [6]. Results clearly show that CPT is higher for samples with higher PMMA content. This indicates that a solution with a higher PMMA proportion has a higher tendency to undergo gelation. This is further discussed in section 5.4.1.

Table 5.2. Cloud point temperatures (CPTs) for various samples (from [6])

Sample ID	CPT (°C)
20PVDF-0PMMA	38-41
19PVDF-1PMMA-120kDa	41-44
19PVDF-1PMMA-35kDa	
18PVDF-2PMMA-35kDa	44-47
18PVDF-2PMMA-120kDa	
16PVDF-4PMMA-35kDa	47-50
16PVDF-4PMMA-120kDa	

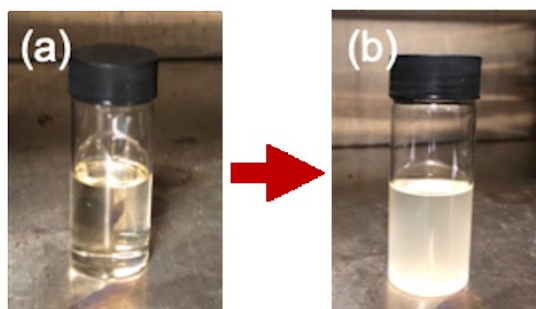


Figure 5.5. (a) Clear polymer solution (b) cloudy solution (from [6])

5.3.5 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Figure 5.6 shows ATR-FTIR spectra for the various samples that were analysed. Since the most important absorbance bands for this study lie in the range of $1800\text{--}650\text{ cm}^{-1}$, the spectra have been presented only for this wavenumber range. Raw polymer powders that were used in the preparation of dope solutions were also analysed for reference. The fingerprint regions for PMMA and different phases of PVDF present in the spectra (Figure 5.6) are presented in Table 5.3 [9, 10].

Table 5.3 Absorbance bands for PMMA and different phases of PVDF with its corresponding wavenumbers (from [6])

Wavenumber (cm^{-1})	Absorbance band
763, 795, 854, 975, 1151, 1207, 1383, 1424	PVDF α phase
1275, 1431	PVDF β phase
1234	PVDF γ phase
839	PVDF β or/and γ phases
877, 1074, 1176, 1401	PVDF (common for all 3 phases)
1718, 1729	PMMA

Absorption bands at 877, 1074, 1176 and 1401 cm^{-1} are common bands that appear for all three phases of PVDF and therefore are observed in the spectra of raw PVDF powder along with that of all the membranes [10]. The spectra of raw PVDF powder indicates mainly the presence of α phase PVDF as its spectrum has absorption bands at 763, 795, 854, 975, 1151, 1207, 1383, 1424 cm^{-1} [10-12]. In contrast to this, the membranes are composed of mainly β

(1275 and 1431 cm^{-1}) and γ (1234 cm^{-1}) phase PVDF with little presence of α phase [9, 10]. In addition to this, absorption bands at 839 cm^{-1} are characteristic of either beta or gamma phases of PVDF or both. Here they represent both these phases and are much deeper in the spectra of membranes compared to that of raw PVDF powder [9, 10, 12].

The prominence of beta and gamma phases is a characteristic of PVDF CCD membranes and also partly responsible for their superior mechanical strengths when compared to the PVDF NIPS membranes, which are composed mainly of the alpha phase PVDF [13, 14].

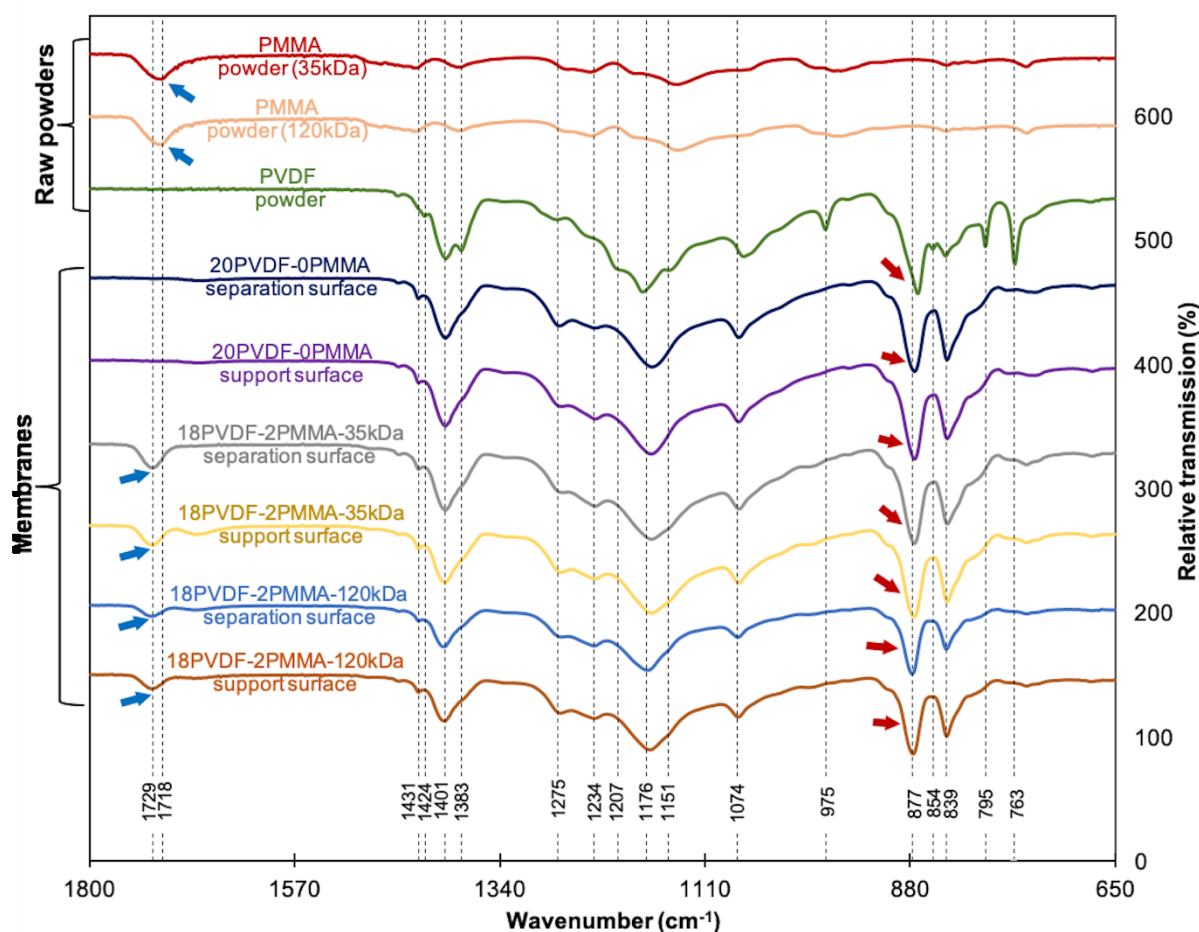


Figure 5.6. ATR-FTIR spectra for the various samples analysed (from [6])

Spectra representing 35kDa and 120kDa PMMA powders show the distinct absorption bands at 1718 cm^{-1} due to the stretching vibration of the C=O group in PMMA. These absorption bands are also visible in the spectra of blend membranes but are slightly shifted to a higher wavenumber (1729 cm^{-1}), just as is seen in other studies involving PVDF-PMMA mixtures [9, 15-19]. This shift is ascribed to the interactions between carbonyl groups of PMMA and CH_2 groups of PVDF and indicates the formation of blends [9, 15].

In addition to identifying these characteristic absorption bands, semi-quantitative analysis is carried out using the ATR-FTIR result, to compare the relative proportion of PVDF to PMMA in the separation and support surfaces of the membranes as a function of the molecular weight of PMMA. ATR-FTIR has a probing depth of about 1-3 μm [20], while the membranes fabricated for this study have a thickness of about 200 μm . This implies that when analysing the separation and support surfaces separately, the properties of the membrane at approximately 1/100th the total membrane thickness from that surface side are reflected in the FTIR spectrum. Therefore, the absorption bands seen in the resultant spectrum would be more representative of that surface side (separation or support). Thus, ATR-FTIR can still be used to provide some surface insights as carried out by several researchers [21-25], although it is understood that XPS is more suited because of its relatively low penetration depth (1-10 nm) [26].

The absorption bands highlighted in blue (1729 cm^{-1}) and red (877 cm^{-1}) shall be used to quantify the relative presence of PMMA and PVDF respectively in the separation/support surfaces of the blend membranes. The absorption band at 877 cm^{-1} is specifically chosen over others for PVDF, as it represents all three phases of PVDF and is least interfered with the troughs and peaks that are found in the spectrums of PMMA.

Table 5.4. Absorption intensities (AIs) for bands representing PVDF and PMMA and its ratio (BIR) as interpreted from the spectra of various membrane samples (from [6])

Sample ID	Membrane surface side	AI _{PVDF} (%)	AI _{PMMA} (%)	BIR
18PVDF-2PMMA-35kDa	separation	81.4	20.2	4.0
	support	73.9	15.8	4.7
18PVDF-2PMMA-120kDa	separation	56.8	9.8	5.7
	support	63.8	11.0	5.8

The band intensity ratios (BIRs), defined here as the ratio of the absorption intensities (AIs) of PVDF to PMMA, are presented in Table 5.4 where 18PVDF-2PMMA-35kDa and 18PVDF-2PMMA-120kDa are chosen as the model pair for comparison purposes [6]. Direct comparison of AIs would be inappropriate as the intensity of the bands can be affected by the force applied by the operator while placing the sample on the crystal probe, which can vary

each time. Similarly, directly comparing the magnitudes of the BIRs (i.e. PVDF to PMMA proportions) of the two different samples would also be inappropriate as the two samples are prepared using different molecular weights of PMMA, obtained from different suppliers, and therefore could influence the band intensities in a way that would distort the quantitative analysis. Instead, the BIR comparison should be limited to that of separation and support surfaces of a single sample only for semi-quantitative analysis. The difference in the BIRs of two surfaces of a sample would therefore be indicative of the difference in the PVDF to PMMA proportion between these surfaces.

BIR value for the support surface is higher than the separation surface by 17% for 18PVDF-2PMMA-35kDa and by 2% for 18PVDF-2PMMA-120kDa. The spectra presented in Figure 5.6 is for only one of the 5 specimens analysed for each sample and so the result presented so far was for only one of these 5 specimens. The process of determining AIs, BIRs and the percentage difference in the BIRs between the two surfaces was repeated for all the specimens. On average, the BIRs for the support surfaces were higher than the BIRs for the separation surfaces by 19% and 7% for 18PVDF-2PMMA-35kDa and 18PVDF-2PMMA-120kDa samples respectively.

This suggests that 18PVDF-2PMMA-35kDa sample has a higher difference in the PVDF to PMMA proportion between the two ends of the membrane compared to 18PVDF-2PMMA-120kDa sample. During the CCD process, directional growth of solvent crystals is accompanied by polymer diffusion from the cold to warm end of the cast film which become the separation and support surfaces of the final membrane respectively [7]. This BIR analysis, therefore suggests that the relative rate of diffusion of PVDF to PMMA is higher for 18PVDF-2PMMA-35kDa compared to 18PVDF-2PMMA-120kDa. With this analysis, we can conclude that by merely changing the molecular weight of the additive (PMMA), one can influence the diffusion rate of the main polymer constituent (PVDF). The implications of this on the pore sizes of the membranes are discussed in section 5.4.2.

5.3.6 Mechanical test

The tensile strength of 20PVDF-0PMMA, 18PVDF-2PMMA-35kDa and 18PVDF-2PMMA-120kDa were measured to gauge the impact of addition of PMMA on the mechanical properties of the membrane. Table 5.5 presents the tensile stress test results for these samples [6]. The membrane thickness hardly varied between samples and remained between 0.18-

0.20mm. PMMA is known for its brittle nature because of its low tensile strength [27], while PVDF is known for its superior mechanical properties with one of the highest tensile strength among polymers [4, 28, 29]. Thus, although it may seem that the presence of PMMA decreases both the tensile strength and the maximum load that the membrane can endure before the rupture, these properties remain within the standard deviation of the measurements.

Table 5.5. Tensile test results for pure PVDF and PMMA blended samples [6].

Sample ID	Thickness (mm)	Tensile strength (MPa)	Maximum load (N)	Percentage strain at maximum extension (%)	Young's modulus (MPa)
20PVDF-0PMMA	0.19 ± 0.01	2.5 ± 0.3	4.8 ± 0.5	30 ± 8	102 ± 13
18PVDF-2PMMA- 35kDa	0.18 ± 0.01	2.1 ± 0.2	4.2 ± 0.4	14 ± 3	101 ± 9
18PVDF-2PMMA- 120kDa	0.20 ± 0.01	1.9 ± 0.3	3.8 ± 0.6	16 ± 5	98 ± 4

The young's modulus, which is a measure of the resistance to elastic deformation under load or in other words, a measure of the stiffness of a material, is very similar for all three samples. This indicates that in the linear elasticity region when the stress is still low, the strain encountered by the membranes remains similar across samples. This is because, at low stresses, the properties of PVDF seem to dominate as even in the blended samples, PVDF constitutes the major proportion of the polymer concentration. As stress is increased, the blend membranes stop yielding and rupture sooner than pure PVDF membranes as shown by the results of maximum strain capacity. This illustrates the practical limitations of using PMMA to adjust the properties of CCD membranes.

5.4 Discussion

5.4.1 Increase in PMMA and a decrease in pore size

The SEM images and the mean flow pore size results indicate that increasing the proportion of PMMA, produces membranes characterised by narrower micro-channels in the support layer and smaller pore sizes in the separation layer. The proposed polymer-solvent binary phase diagram for CCD method, as illustrated earlier in Figure 2.8 in section 2.11.3, can be used to explain this trend. It is represented here again as Figure 5.7.

Table 5.6. Hansen solubility parameters for PVDF, PMMA and DMSO (from [6])

Material	δ_d (MPa ^{0.5})	δ_p (MPa ^{0.5})	δ_{hb} (MPa ^{0.5})	$\delta_{t,P-S}$ (MPa ^{0.5})
DMSO ^a	18.4	16.4	10.2	N/A
PVDF ^a	17.2	12.5	9.2	4.2
PMMA ^b	17.8	9.2	5.5	8.6

^a For DMSO and PVDF, the values are obtained from [30].

^b For PMMA, the values are obtained from [31]. Average values presented here.

Table 5.6 shows Hansen solubility parameters for PMMA, PVDF and DMSO [6, 30, 31]. Hansen solubility parameters have proven to be a powerful way to predict compatibility between polymer and solvent [32]. The three parameters, δ_d , δ_p and δ_{hb} , represent the energy between molecules from dispersion forces, dipolar intermolecular forces and hydrogen bonds respectively. To gauge the compatibility between polymer and solvent, Hansen suggests calculating $\delta_{t,P-S}$, which represents the distance between polymer (P) and solvent (S) coordinates in a three-dimensional δ_d , δ_p , δ_{hb} Hansen space, using Equation 5.1 [30]. These are computed for PMMA-DMSO and PVDF-DMSO and presented in the last column of Table 5.6. Lower the distance $\delta_{t,P-S}$, more favourable the interactions would be between the polymer and the solvent.

$$\delta_{t,P-S} = \sqrt{(\delta_{d,P} - \delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 + (\delta_{hb,P} - \delta_{hb,S})^2} \quad \text{Equation 5.1}$$

The distance $\delta_{t,P-S}$ for PMMA-DMSO is more than double that for PVDF-DMSO, which clearly indicates that the interactions between molecules of the former pair are considerably less favourable which would, therefore, reflect in its compatibility with each

other. This suggests that an increase in the proportion of PMMA, while still maintaining the total polymer content at 20wt.%, may increase the tendency of the solution to undergo gelation sooner. The increase in the cloud point temperatures of the solution with increasing PMMA proportion, as was seen in section 5.3.4, also suggested the same trend. Therefore, from a thermodynamic standpoint, the addition of PMMA may shift the gelation curve leftwards as shown in Figure 5.7, such that when the solvents are crystallising, the polymer solution reaches the gelation phase sooner, and therefore limits the size to which the crystals can grow.

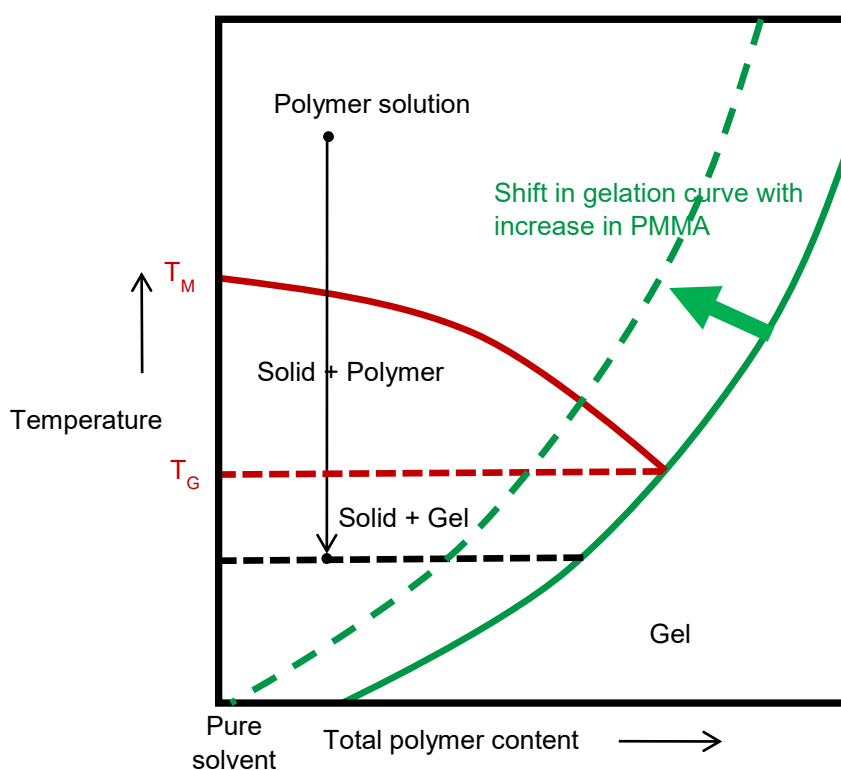


Figure 5.7. Binary phase diagram proposed for CCD method showing the shift in gelation curve (from [6])

From the kinetic standpoint as well, because of not so favourable interactions between PMMA and DMSO, the PMMA molecules will eject out faster from the growing solvent crystal, and form a particle-like conformation in the solution surrounding the crystal. These conformations shall have slower diffusion rates and therefore present steric hindrances to DMSO and polymer molecules that diffuse in and out of solvent crystal for its growth. Additionally, owing to the not so favourable interactions and increased instability of PMMA in DMSO as witnessed by cloud point temperature results, the viscosity of the solution with

higher PMMA content may also be higher and thereby retard the diffusion rate further. As a result, the overall diffusion rate of all the molecules is slowed down, leading to a polymer concentration spike in the solution surrounding the crystal. This causes the polymer solution to meet the gelation point sooner, thereby reducing the time for and extent of crystal growth.

Thus, the compounded effect of change in thermodynamic and kinetic properties causes the solution with a higher proportion of PMMA to form smaller sized crystals resulting in smaller pore sizes and narrower microchannels.

5.4.2 Higher molecular weight of PMMA and smaller pore size

The results also show that blend membranes prepared using higher molecular weight PMMA (120kDa) have smaller pore sizes compared to those made using lower molecular weight PMMA (35kDa). This effect of the molecular weight of PMMA on the pore sizes can be attributed to a change in the diffusion rates of the molecules.

The CCD method involves unidirectional cooling of the polymer cast film, which initiates the freezing and crystallisation of solvent molecules from the cold end of the membrane. A frozen front of solvent crystals that develops at this end progressively moves towards the other end [7, 13]. Preceding the moving frozen front would be a region of high polymer concentration formed as a result of the polymer molecules that are ejected out from the solvent crystals that are part of the frozen front. This, in turn, causes these polymer molecules to diffuse towards the other end, away from the frozen front. As the frozen front grows, more polymer molecules are ejected out from the solvent crystals, which then diffuse away. In the final membrane, the relatively cold and warm ends represent the separation and support sides respectively. As was explained earlier, PMMA as a compound itself is not very compatible with DMSO, and therefore reduces the diffusion rates of polymer and solvent molecules by presenting steric hindrances.

Evidence gathered from ATR-FTIR results suggested a slower diffusion rate of PVDF relative to PMMA in the case of 18PVDF-2PMMA-120kDa compared to 18PVDF-2PMMA-35kDa. Since the diffusion of 120kDa PMMA itself be slower than 35kDa PMMA, owing to its longer chain length [33], it would have a cascading effect on the diffusion rate of PVDF based on the ATR-FTIR results. As a result, the overall diffusion rates of all the molecules would be slower in 18PVDF-2PMMA-120kDa than in 18PVDF-2PMMA-35kDa and also result in additive enrichment near the separation layer more prominently in the former than the

latter. Slower diffusion rates result in smaller crystal sizes as was explained earlier, which then ultimately reflect in the final membrane as smaller pore sizes.

5.4.3 Increase in PMMA and maintained PWP

Although an increase in PMMA proportion from 1 to 4 wt.% decreases the mean flow pore sizes, the PWP remains almost constant. Typically, with a decrease in pore sizes, the PWP also decreases; however, this is not the case for these PVDF-PMMA blended membranes prepared via CCD. This is because, with an increase in the PMMA dosage, although the mean flow pore size decreases, the membrane porosity increases, as was seen in the results presented in section 5.3.3.

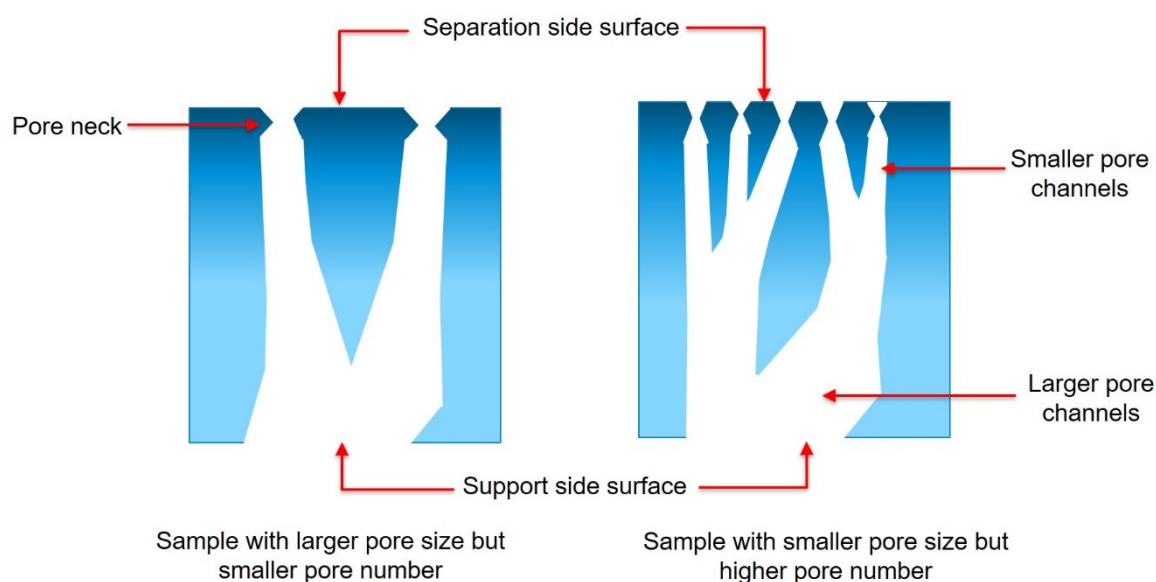


Figure 5.8. Schematic illustrating the pore structure of CCD blend membranes as influenced by the pore size and the pore number (from [6])

During cooling of a pure PVDF dope in a typical CCD process, homogenous nucleation of solvent takes place in the cold end of the cast film, which then grows heterogeneously towards the other end of the membrane, forming a columnar and dendritic structure. Heterogeneous nucleation is generally preferred as it has a lower energy barrier and requires a lower degree of undercooling but is only initiated in the presence of a surface of a wall or an existing crystal [7]. The presence of impurities, such as small particles, can also act as heterogeneous nucleation centres, and the number of nuclei will depend on the impurity concentration [34, 35]. Due to the low compatibility of PMMA with DMSO as explained earlier, PMMA is likely to adopt particle-like conformations in the dope which shall act as

nucleation centres. A higher concentration of PMMA will result in more nucleation centres and therefore result in a higher number of pores. While for PVDF, its molecules will adopt a chain-like conformation and cannot act as the nucleation centre, therefore it would not directly affect the pore number. Thus, the effect of smaller pore sizes in membranes prepared with a higher PMMA proportion, be compensated by an increase in the number of pores and its channels to keep the PWP effectively constant. This has been illustrated in Figure 5.8 which shows an increase in the number of pore channels for the sample with smaller pore size [6].

5.5 Dual-casting

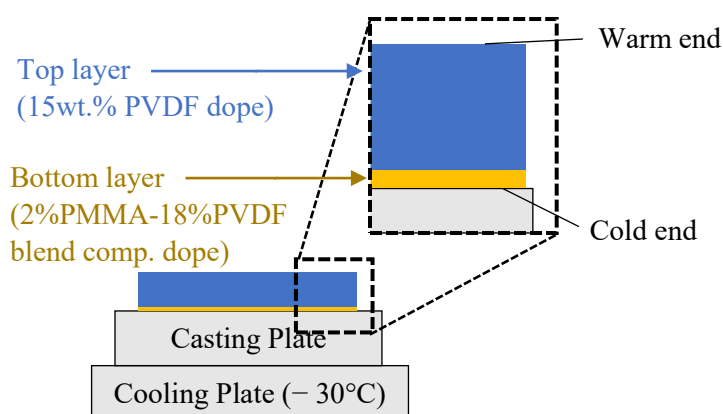


Figure 5.9. Schematic showing the dual-casting arrangement with the blend dope composition

Dual-casting which was applied in the previous chapter was also applied to PVDF-PMMA blend membranes. The casting thicknesses were the same as those used earlier in section 4. The aim was to keep the pore sizes still as small as that obtained by the blend membranes, but enhance the permeabilities even further. The bottom thinner layer was cast using the blend composition dope (18wt.% PVDF, 2wt.% 120 kDa PMMA and 80wt.% DMSO) while the top thicker layer was cast using 15wt.% dope. The schematic of this is shown in Figure 5.9. The prepared membrane shall be referred to as Dual_18PVDF-2PMMA-120kDa_15PVDF. The PWP and mean flow pore size results of this membrane are compared to its single-cast counterpart 18PVDF-2PMMA-120kDa and presented in Figure 5.10.

The results show almost a two-fold increase in PWP in the dual-cast membrane compared to its single-cast counterpart, without any increase in its mean flow pore size. The slight reduction in mean flow pore size in the dual-cast membrane could be the result of external factors such as the outside room temperature which could influence the solvent crystallisation

process on that day and result in slightly varied pore sizes. The result shows that dual-casting is indeed effective in allowing one to maintain the pore sizes while enhancing the membrane permeances. This dual-cast CCD membrane also does not suffer from any delamination and appears as a single integral membrane as seen in the SEM image of the membrane cross-section shown in Figure 5.11-b. The separation surface (Figure 5.11-a) of the dual-cast membrane resembles that of its single-cast counterpart but has a support layer that is much more porous. The SEM images of the single-cast membrane were presented earlier in Figure 5.1.

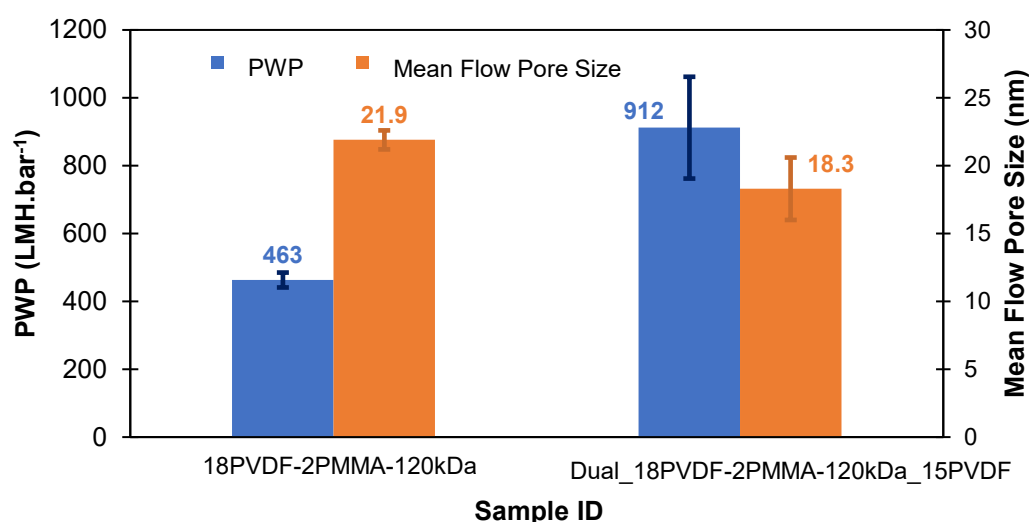


Figure 5.10. PWP (left axis) and Mean Flow Pore Size (right axis) for single-cast (18PVDF-2PMMA-120kDa) and dual-cast (Dual_18PVDF-2PMMA-120kDa_15PVDF) membranes

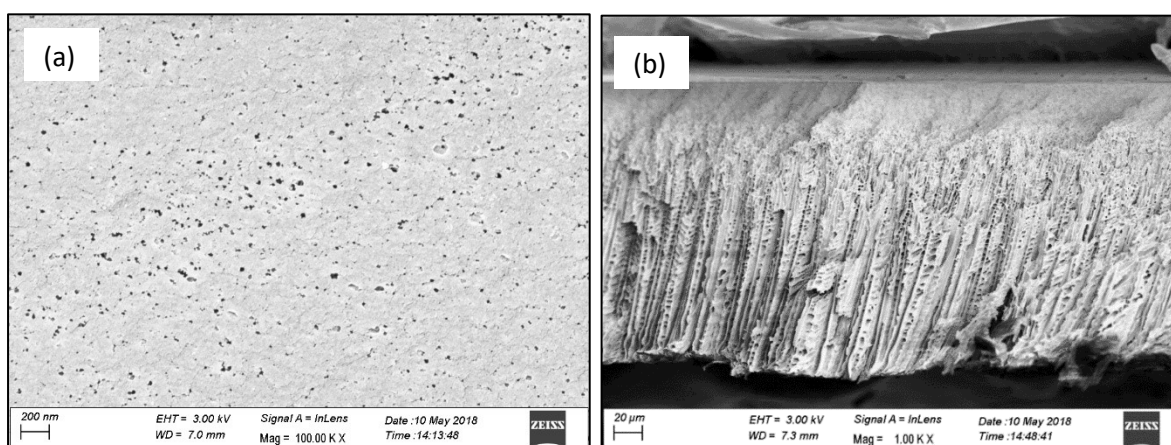


Figure 5.11. SEM images of (a) separation surface and (b) cross-section of Dual_18PVDF-2PMMA-120kDa_15PVDF

Table 5.7 summarises the effect of PMMA addition and dual-casting technique on the pore sizes and pure water permeances of the prepared membranes. Just as dual-layer casting worked effectively in enhancing the PWP of pure PVDF membranes, it works equally well for the blend samples. In both the scenarios, the dual casting helps in improving the PWP by around 100%. Thus, on comparing the two samples, 20PVDF-0PMMA and Dual_18PVDF-2PMMA-120kDa_15PVDF, despite a significant reduction in the pore size, the reduction in PWP is only marginal. As a result, for the given pore size ranges, these blend PVDF-CCD membranes also continue to have much higher permeances than the PVDF membranes that are traditionally prepared in academia and industry (Table 2.2 and Table 2.3 in section 2.10).

Table 5.7. Summary of mean flow pore sizes and pure water permeances of pure and blend single-cast PVDF membranes with their dual-cast counterparts

Dope solution type	Sample ID	Casting type	Mean flow pore size (nm)	PWP (LMH.bar⁻¹)
Pure PVDF	20PVDF-0PMMA	Single-cast	33 ± 2	1295 ± 120
	20PVDF_15PVDF_CCD	Dual-cast	32 ± 1	2383 ± 216
PVDF-PMMA blend	18PVDF-2PMMA-120kDa	Single-cast	22 ± 1	463 ± 22
	Dual_18PVDF-2PMMA-120kDa_15PVDF	Dual-cast	18 ± 2	912 ± 150

5.6 Conclusion

In this study, PMMA was added as an additive to PVDF-DMSO dope solutions to decrease the pore size of PVDF CCD membranes. The addition of PMMA to pristine PVDF does decrease the mean flow pore size and the PWP, however, further increase in the proportion of PMMA keeps the PWP levels maintained, while further reducing the pore size. The decline in permeance was much more serious in the 25PVDF-0PMMA sample compared to other blend membranes, which suggested that simply increasing polymer dope concentration is not an effective way to reduce membrane pore size and that the blending approach is much more efficient.

Furthermore, of the two molecular weight sizes of PMMA chosen (120kDa and 35kDa) for the preparation of blend membranes, the ones prepared using higher molecular weight

PMMA, showed smaller pore sizes and poorer PWP. SEM images also showed narrower micro-channels in the support layer of the blend membranes. ATR-FTIR detected the presence of PMMA and identified various phases of PVDF. The absorption band intensities and cloud point temperature results provided insights about kinetic and thermodynamic factors underplay, which affects the final membrane properties. The tensile strength and strain capacity also reduced with the addition of brittle PMMA.

The findings indicate that CCD as a platform membrane manufacturing technique can be fine-tuned to produce membranes with varied characteristics, by manipulating influencing factors based on the formation mechanism, which is starkly different from the NIPS and TIPS techniques. One of the findings illustrated the possibility to selectively alter the membrane surface properties through the controlled distribution of functional additives with the CCD technique by a simple blending approach. By combining the PMMA blending with the dual-layer casting approach, the permeation properties can be enhanced even further while still maintaining the pore sizes.

5.7 References

1. Milo, R. and R. Phillips, *Cell Biology by the Numbers*. 2015: CRC Press.
2. Ochoa, N.A., M. Masuelli, and J. Marchese, *Effect of hydrophilicity on fouling of an emulsified oil wastewater with PVDF/PMMA membranes*. Journal of Membrane Science, 2003. **226**(1): p. 203-211.
3. Nunes, S.P. and K.V. Peinemann, *Ultrafiltration membranes from PVDF/PMMA blends*. Journal of Membrane Science, 1992. **73**(1): p. 25-35.
4. Pfenning, A., *Kirk-Othmer Encyclopedia of Chemical Technology*. 1995: Weinheim. p. 1022-1022.
5. Uragami, T., Y. Naito, and M. Sugihara, *Studies on synthesis and permeability of special polymer membranes*. Polymer Bulletin, 1981. **4**(10): p. 617-622.
6. Shah, V., B. Wang, and K. Li, *Blending modification to porous polyvinylidene fluoride (PVDF) membranes prepared via combined crystallisation and diffusion (CCD) technique*. Journal of Membrane Science, 2021. **618**: p. 118708.
7. Wang, B., et al., *Porous membranes prepared by a combined crystallisation and diffusion (CCD) method: Study on formation mechanisms*. Journal of Membrane Science, 2018. **548**: p. 136-148.

8. Tanis-Kanbur, M.B., et al., *Membrane characterization via evapoporometry (EP) and liquid-liquid displacement porosimetry (LLDP) techniques*. Journal of Membrane Science, 2019. **586**: p. 248-258.
9. Mohamadi, S., *Preparation and Characterization of PVDF/PMMA/Graphene Polymer Blend Nanocomposites by Using ATR-FTIR Technique*, in *Infrared Spectroscopy - Materials Science, Engineering and Technology*. 2012.
10. Cai, X., et al., *A critical analysis of the α , β and γ phases in poly(vinylidene fluoride) using FTIR*. RSC Advances, 2017. **7**(25): p. 15382-15389.
11. Ai, F., et al., *Surface characteristics and blood compatibility of PVDF/PMMA membranes*. Journal of Materials Science, 2012. **47**(12): p. 5030-5040.
12. Li, Y., et al., *How Chain Intermixing Dictates the Polymorphism of PVDF in Poly(vinylidene fluoride)/Polymethylmethacrylate Binary System during Recrystallization: A Comparative Study on Core-Shell Particles and Latex Blend*. Polymers, 2017. **9**(9): p. 448.
13. Wang, B., J. Ji, and K. Li, *Crystal nuclei templated nanostructured membranes prepared by solvent crystallization and polymer migration*. Nat Commun, 2016. **7**: p. 12804.
14. Haponska, M., et al., *PVDF Membrane Morphology—Influence of Polymer Molecular Weight and Preparation Temperature*. Polymers, 2017. **9**(12).
15. Elashmawi, I.S. and N.A. Hakeem, *Effect of PMMA addition on characterization and morphology of PVDF*. Polymer Engineering & Science, 2008. **48**(5): p. 895-901.
16. Rajabzadeh, S., et al., *Preparation of PVDF/PMMA blend hollow fiber membrane via thermally induced phase separation (TIPS) method*. Separation and Purification Technology, 2009. **66**(1): p. 76-83.
17. Mahant, Y.P., et al., *Electrospun Poly (Vinylidene Fluoride)/Poly (Methyl Methacrylate) Composite Nanofibers Polymer Electrolyte for Batteries*. Procedia Materials Science, 2015. **10**: p. 595-602.
18. Aziz, S.B., et al., *From Insulating PMMA Polymer to Conjugated Double Bond Behavior: Green Chemistry as a Novel Approach to Fabricate Small Band Gap Polymers*. Polymers (Basel), 2017. **9**(11).
19. Zhang, H.P., et al., *A novel sandwiched membrane as polymer electrolyte for lithium ion battery*. Electrochemistry Communications, 2007. **9**(7): p. 1700-1703.

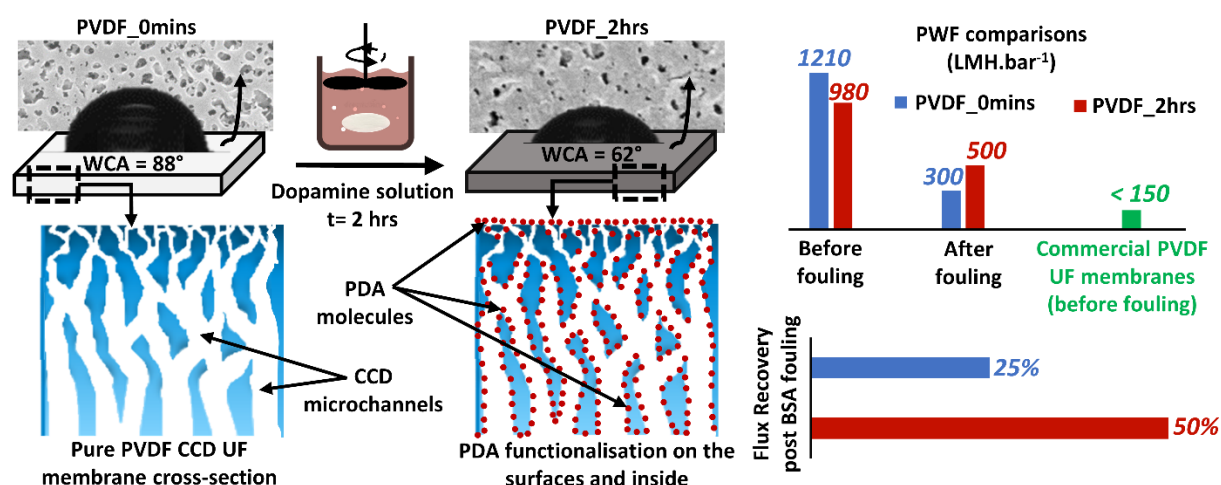
20. Andrew Chan, K.L. and S.G. Kazarian, *Attenuated total reflection Fourier-transform infrared (ATR-FTIR) imaging of tissues and live cells*. Chemical Society Reviews, 2016. **45**(7): p. 1850-1864.
21. Belfer, S., Y. Purinson, and O. Kedem, *Surface modification of commercial polyamide reverse osmosis membranes by radical grafting: An ATR-FTIR study*. Acta Polymerica, 1998. **49**(10-11): p. 574-582.
22. Peyravi, M., et al., *Tailoring the surface properties of PES ultrafiltration membranes to reduce the fouling resistance using synthesized hydrophilic copolymer*. Microporous and Mesoporous Materials, 2012. **160**: p. 114-125.
23. Rahimpour, A., *UV photo-grafting of hydrophilic monomers onto the surface of nanoporous PES membranes for improving surface properties*. Desalination, 2011. **265**(1): p. 93-101.
24. Belfer, S., et al., *Surface characterization by FTIR-ATR spectroscopy of polyethersulfone membranes-unmodified, modified and protein fouled*. Journal of Membrane Science, 2000. **172**(1): p. 113-124.
25. Hsiue, G.-H., et al., *Surface characterization and biological properties study of silicone rubber membrane grafted with phospholipid as biomaterial via plasma induced graft copolymerization*. Journal of Biomedical Materials Research, 1998. **42**(1): p. 134-147.
26. Crompton, T.R. and R.T. Limited, *Polymer Reference Book*. 2006: Rapra Technology Limited.
27. Dixit, M., et al., *Morphology, miscibility and mechanical properties of PMMA/PC blends*. Phase Transitions, 2009. **82**(12): p. 866-878.
28. Crompton, T.R., *Physical Testing of Plastics*. 2012: Smithers Rapra.
29. Enzo, G., *Semi-crystalline fluorinated polymers*. Polymer International, 2001. **50**(1): p. 10-26.
30. Bottino, A., et al., *The formation of microporous polyvinylidene difluoride membranes by phase separation*. Journal of Membrane Science, 1991. **57**(1): p. 1-20.
31. Lindvig, T., M.L. Michelsen, and G.M. Kontogeorgis, *A Flory–Huggins model based on the Hansen solubility parameters*. Fluid Phase Equilibria, 2002. **203**(1): p. 247-260.
32. Wypych, G., *Handbook of Solvents*. 2001: Noyes Publications.
33. Morris, B.A., *The Science and Technology of Flexible Packaging: Multilayer Films from Resin and Process to End Use*. 2016: Elsevier Science.

34. Goldstein, V.Y. and V.Y. Novikov, *Heterogeneous nucleation in crystallization: Impact of impurities and local melt inhomogeneity*. Materials Letters, 2018. **229**: p. 164-166.
35. Binsbergen, F.L., *Heterogeneous nucleation in the crystallization of polyolefins. III. Theory and mechanism*. Journal of Polymer Science: Polymer Physics Edition, 1973. **11**(1): p. 117-135.

6 PVDF-CCD Polydopamine modification of high-performance PVDF ultrafiltration membranes prepared by the Combined Crystallisation and Diffusion (CCD) method

Abstract

Polyvinylidene fluoride (PVDF) membranes produced by the CCD method have pure water permeances that are a magnitude higher than those produced via conventional membrane manufacturing technology. However, most of the PVDF CCD membranes so far produced are hydrophobic, easy to be fouled in filtration applications. Herein, we applied the popular polydopamine (PDA) modification technique to improve the hydrophilicity of PVDF CCD membranes to ensure that their high permeation performance is maintained even in foulant-rich environments. Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray (EDX) analysis were used as characterisation techniques to understand the dynamics of the PDA deposition process. The results showed that an increase in modification time does clearly improve the membrane surface hydrophilicity, but suffers in its permeance, as an inevitable consequence of the increased pore blockage by the deposited PDA layer. Because of this, even in the fouling studies, the sample modified for a shorter duration (2hours) and not longer duration (12hours or 24hours) showed the best overall permeation performance. The permeation results from the fouling study present PDA-modified PVDF CCD membranes as promising alternatives to many of the well-established industry-standard membranes.



Keywords: PVDF membrane, Ultrafiltration, Crystallisation, Fouling, Polydopamine

6.1 Introduction

The previous chapters showcased the ability to effectively control the permeation and separation performance of PVDF CCD membranes. Despite these advantages, PVDF as a material itself is hydrophobic in its natural form and thus its membranes are highly susceptible to fouling during filtration applications [1-3]. Most often, membrane fouling is the result of irreversible adsorption of the foulant onto the hydrophobic membrane surface. Many times, these foulants cannot be removed out through simple physical cleaning [3, 4]. As a consequence of this, the permeation performance of membranes deteriorates quite significantly. Many modifications techniques exist today to improve the hydrophilicity and in turn the anti-fouling capability of PVDF membranes [5-7]. These modification techniques can be broadly categorised into either blending or surface modifications [5, 6].

Blending modification involves blending the main polymer dope solution with either a hydrophilic polymer (like PVP, PEG, PMMA etc.) [8-12], or an amphiphilic copolymer (like PVDF-g-PEGMA¹, PVDF-g-PMAA², PVDF-g-PSBMA³ etc.) [13-31]. The membranes are then prepared via the usual fabrication route. The intention is to self-assemble these hydrophilic polymers or hydrophilic parts of the amphiphilic copolymers at the surface which then renders the surface hydrophilic. Sometimes inorganic nanoparticles (such as TiO₂, SiO₂, Al₂O₃, carbon nanotubes, graphene oxide etc.) are also used as blending additives usually in high proportions to make mixed matrix membranes with specialised properties [6, 32-42].

Surface modification is carried out post membrane fabrication and can be carried out either through physical deposition or through chemical treatment [6]. Physical modification would involve depositing a hydrophilic polymer on the membrane surface (such as PVA [43], chitosan [44] or amphiphilic copolymers [45, 46]) which is followed additional treatment sometimes [47-49]. Chemical modification on the other hand would involve modification of the membrane surface through covalent bonding interaction and therefore provides long-term chemical stability compared to physical modification techniques. Chemical modification is usually carried out by pre-activation of the PVDF chains by a chemical reaction or high-energy radiation and then followed by grafting hydrophilic modifiers on its surface [49-69].

¹ PEGMA = Poly(ethylene glycol) methyl ether methacrylate

² PMAA = Poly(methacrylic acid)

³ PSBMA= Poly(sulfobetaine methacrylate)

Blending modification most often undesirably affects the membrane morphology in addition to influencing the surface hydrophilicity. Surface modification on the other hand may specifically target the surface and keep the internal membrane morphology intact. While physical surface modification may be simple to implement, it may not provide long term stability. The chemical surface modification on the other hand may require specialised chemicals and sophisticated apparatus. As a result, many of these modification techniques may also not be implementable on a large scale for commercial application.

One of the surface modifying techniques that were not mentioned above was using polydopamine (PDA), a newly discovered bio-inspired polymer that non-selectively and permanently adheres to virtually any surface and renders it hydrophilic [70-72]. The modification process is extremely simple since it only requires the exposure of the substrate to an alkaline solution of dopamine, in the presence of air, for an adjustable period of time [72]. The formation of PDA on the surface is then the result of the oxidative polymerisation of dopamine [73]. Although the exact formation mechanism of PDA remains unknown, the process simplicity, low cost and applicability to a wide range of substrates has increased the popularity of the PDA modification technique in recent years. Besides the bond strength between PDA and its substrate is expected to be as strong as covalent interactions [3, 10, 11] which ensures the robustness of the coatings. This technique therefore offers the combined advantages of the physical and chemical modification routes. PDA modification has also been successfully carried out on NIPS-PVDF membranes that are either prepared in the lab or obtained commercially [2, 74-79].

In this study, we aim to modify the surface of PVDF CCD membranes using PDA to make them more hydrophilic and ensure their permeation performance does not deteriorate significantly during filtration applications. The impact of the dopamine solution immersion time on these self-fabricated membranes is systematically studied. The modified membranes are then comprehensively studied for their surface morphology, deposited dopamine composition, permeance and surface hydrophilicity. Simulated fouling tests are carried out using bovine serum albumin (BSA) to gauge the fouling susceptibilities of the modified membranes.

6.2 Experimental Materials and Methods

6.2.1 Materials

Most of the chemicals required for making and characterising PVDF CCD membranes were already mentioned in section 3.1. Additional chemicals used in this study include Tris(hydroxymethyl)aminomethane (Tris base) and dopamine hydrochloride. These were purchased from Merck Sigma Aldrich and used for the PDA treatment of the PVDF CCD membranes. Isopropanol (GPR) was purchased from VWR, UK and was used to remove out any loosely bound PDA from the surface of the membrane post its modification.

6.2.2 Membrane Preparation and PDA Modification

20wt.% PVDF dope solutions in DMSO were used to prepare flat sheet CCD membranes following the procedure described in section 4.2.2.

After membrane fabrication, samples with a diameter of 2.6 cm were cut and stored in water for PDA treatment. Employing a method as suggested in the seminal work on PDA by Lee et al. [71], a concentration of 2g.L^{-1} of dopamine hydrochloride was added to 150 ml of 20mM tris solution in a 400 ml glass beaker. The solution was stirred using an overhead stirrer at a slow speed (100 RPM) to facilitate oxygen diffusion. After 60 secs, when the colourless solution started to turn light brown, three wet membrane samples were added to the glass beaker to commence the adhesion and polymerisation of PDA onto the membrane. The membranes are free to move around in the solution and so functionalisation takes place from both sides. In about 2 mins, the brown solution starts to turn black, suggesting the successful formation of PDA (See Appendix C) [80]. Various batches of PDA-modified membranes were prepared with varying immersion times (0 mins, 15mins, 30 mins, 45 mins, 1 hr, 2 hrs, 5 hrs, 8 hrs, 12 hrs, 24 hrs and 50 hrs). After completion of PDA deposition for a set immersion time, the samples were rinsed using deionised water and then placed in isopropanol overnight to remove any loosely bound PDA.

The samples modified with PDA for a given immersion time have been codenamed as PVDF_“immersion time”. For example, a sample modified with PDA with an immersion time of 2 hours will be referred to as PVDF_2hrs.

6.2.3 Membrane Characterisation

The microstructure of the samples was analysed through SEM following the procedure elaborated in section 3.3, except for these samples the elemental distributions were also determined using an EDX (Energy Dispersive X-Ray) detector. The determination of mean flow pore sizes, through-pore membrane porosities φ and pure water permeances along with the ATR-FTIR spectral analysis of the samples was carried out following the procedure detailed previously in section 3.3.

In addition to the through-pore porosity φ , another measure of porosity was analysed using the SEM micrographs of the separation surfaces of the PDA-modified samples. Image threshold enhancement was applied on the SEM micrographs using the ImageJ software [81], where the pore areas were contrasted sharply against the non-porous surface area. The porosity was then approximated using Equation 6.1. This porosity is referred to as the surface porosity φ_{SEM} to distinguish from the through-pore membrane porosity φ .

$$\varphi_{SEM} = \frac{\text{Total pore area as seen on the surface}}{\text{Total surface area}} \quad \text{Equation 6.1}$$

The membrane surface hydrophilicity was characterised using water contact angles measured using the Ramé-hart Model 590 Advanced Automated Goniometer (See Appendix B6). A 6 μl deionised water droplet was placed on the surface and the WCA was measured using the sessile drop method. The image was captured by the camera in real-time and analysed by the DROPImage Advanced software for the water contact angle. For each sample, the drop in WCA was measured overtime for 250 secs. This was repeated thrice for every sample to ensure consistency in measurements. The value reported in this study is the initial WCA, which is an average of the first 10 secs.

6.2.4 Membrane Fouling tests

BSA is a model protein that is typically used to study the fouling tendency of membranes [25, 82-85]. PDA-modified membrane samples of 4.6 cm diameter were used for the BSA fouling test so that they could fit the cross-flow filtration cell (CF042 Crossflow Assembly, Sterlitech Corporation, USA) (See Appendix B-7) [86]. The PDA modification on the larger sized membranes was performed just as before with immersion times of 0 mins, 2 hrs, 12 hrs and 24 hrs.

At first, each sample was placed in a cross-flow cell and measured for its pure water permeance value. This value is referred to as 'PWP₀'. Following this, the first cycle of the fouling test was carried out. Aggravated cross-flow setup was used for the fouling study, as opposed to tangential cross-flow, to accelerate the membrane fouling (see 6.2.4 and Appendix B-7). BSA aqueous solution of 1g.L⁻¹ concentration was circulated on the feed side of the cross-flow cell with an average flowrate of 300 ml.min⁻¹ and transmembrane pressure of 1 bar. The permeate volume was collected over a mass balance that would log the data continuously to measure the permeance, referred to as 'BSA_Permeance₁', over time. After the completion of the first fouling test cycle lasting 30 mins, the membrane was removed from the cross-flow cell and physically cleaned in an ultrasonic bath for 30 mins. To clean the cross-flow cell (without the membrane) of any residual BSA, 1M sodium hydroxide solution was circulated around in the empty cell for 10 mins followed by the circulation of fresh batches of deionised water until the pH comes back to neutral. Pure water permeance was measured again to evaluate the membrane recovery post fouling. This value is then referred to as 'PWP₁'. The fouling and pure water permeance recovery cycles were repeated again to obtain the 'BSA_Permeance₂' and 'PWP₂' over time. The permeate volume was collected at the end of each fouling cycle. The BSA concentrations in the permeate (C_p) and the feed tank (C_f) were then measured using a UV-VIS spectrophotometer (NanoDrop™ 2000, ThermoFisher Scientific, UK) (See Appendix B8). This then allowed us to compute the BSA rejections 'R_n' using Equation 6.2 [25], where n is the fouling cycle number (1 or 2).

$$R_n = 1 - \frac{C_{p,n}}{C_{f,n}} \quad \text{Equation 6.2}$$

The irreversible (F_{ir,n}) and reversible (F_{r,n}) fouling factors and permeance recovery ratios (PRR_n) were also computed using the following equations [25, 87], where n is the fouling cycle number (1 or 2):

$$F_{ir,n} = \frac{PWP_0 - PWP_n}{PWP_0} \quad \text{Equation 6.3}$$

$$F_{r,n} = \frac{PWP_n - \text{BSA_Permeance}_n}{PWP_0} \quad \text{Equation 6.4}$$

$$PRR_n = \frac{PWP_n}{PWP_0} \quad \text{Equation 6.5}$$

6.3 Results and Discussion

6.3.1 Membrane Morphology, PDA composition and Surface Hydrophilicity

The first signs of successful PDA deposition onto the membrane surface can be visually inferred from the change in membrane colour from white to black as shown in Figure 6.1. FTIR spectroscopy then provides a more thorough conclusion of successful PDA deposition, by identifying the characteristic absorption bands. The characteristic bands of PDA lie in the wavenumber range of $1450\text{--}4000\text{ cm}^{-1}$ and so for clarity, the FTIR spectra in Figure 6.2 are only presented for this range. The broad band peaking at around 3300 cm^{-1} represents the stretching vibrations of N-H and O-H bonds found in PDA. In addition, two other bands representing the C=C and C=N resonance vibrations of the aromatic amine present in PDA are observed at 1594 cm^{-1} and 1506 cm^{-1} wavenumbers respectively. From the result, it can also be seen that the intensities of these absorption bands increase with an increase in immersion time. This, therefore suggests an increase in the PDA concentration in the membranes that are modified for longer times.

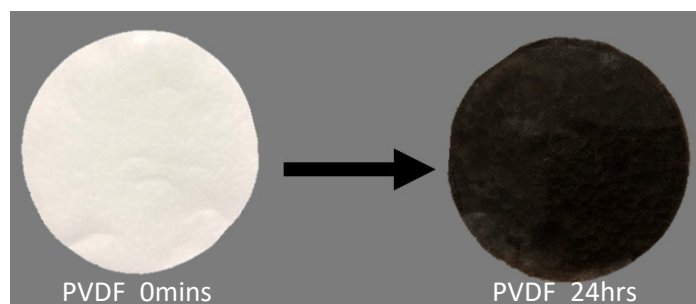


Figure 6.1. Change of colour in PVDF membrane from white to black as a result of PDA deposition

Meanwhile, the characteristic absorption bands for PVDF fall in the wavenumber range of $650\text{--}1450\text{ cm}^{-1}$. The related spectra are presented in Figure 6.3. The FTIR spectrum for PVDF CCD membranes was already discussed in substantial detail earlier in section 5.3.5. In line with those results, here too β and γ phases of PVDF predominate over the α phase, a feature that is a characteristic of CCD membranes [86, 88]. From the perspective of PDA deposition, the absorption band depths of various PVDF crystal phases hardly change with increasing immersion time in dopamine solution. It can therefore be concluded that the original PVDF membrane crystallinity remains unaffected by this external PDA modification process.

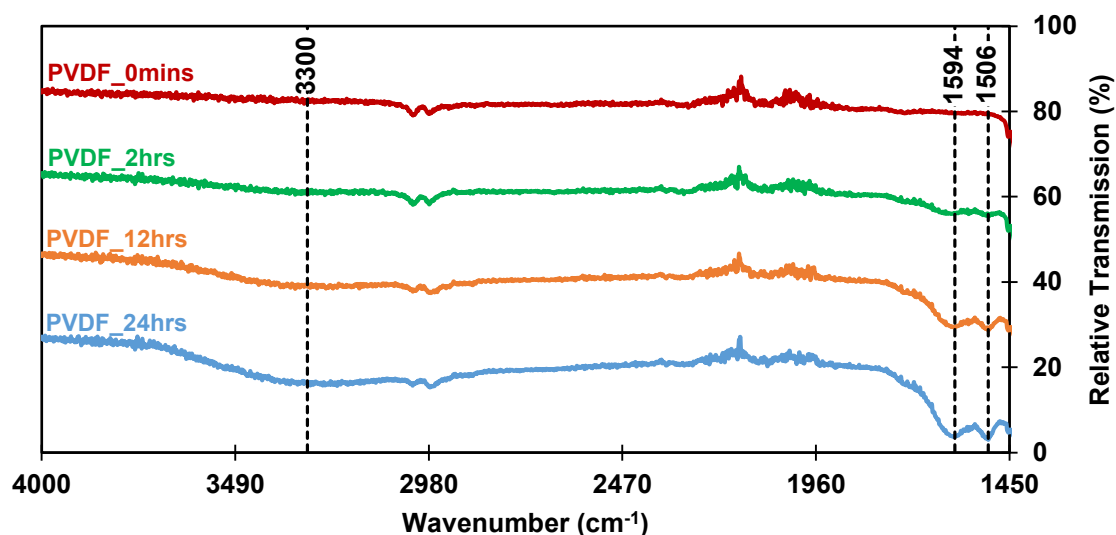
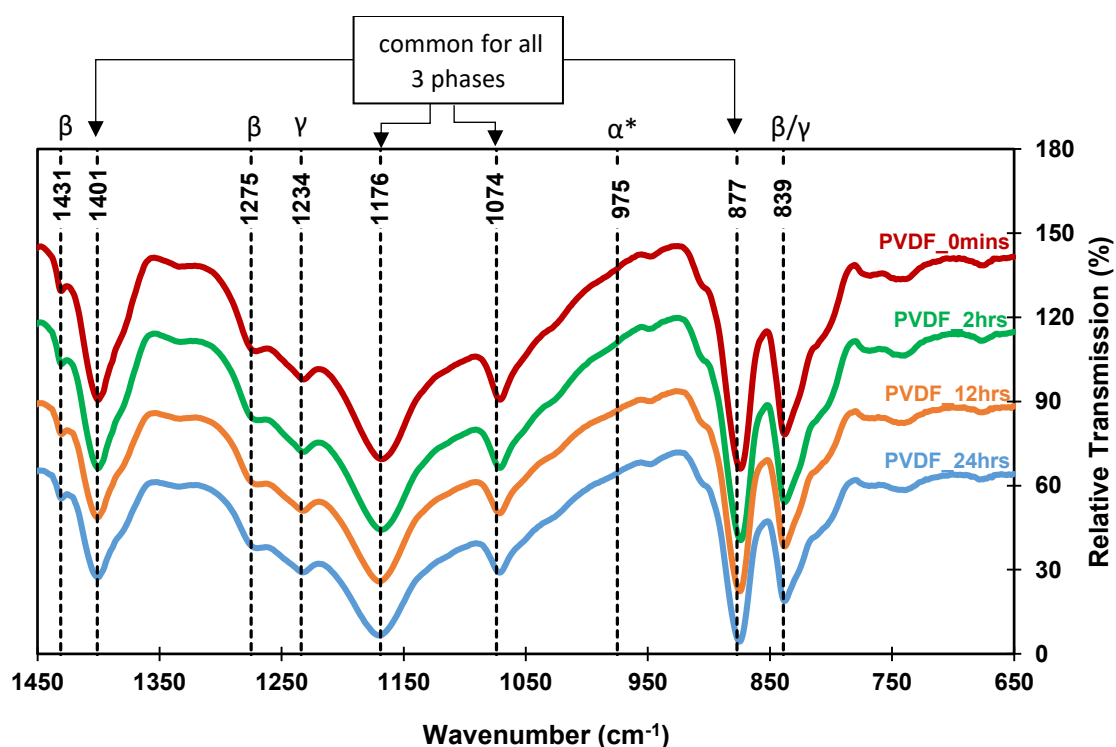


Figure 6.2. ATR-FTIR spectra of various PDA-modified PVDF samples from 4000 to 1450 cm^{-1} showing the characteristic absorption bands for PDA



*The characteristic fingerprint regions for α phase are many, but only one at 975 cm^{-1} is presented here.

Figure 6.3. ATR-FTIR spectra of various PDA-modified samples from 1450-650 cm^{-1} showing the different characteristic absorption bands for different phases of PVDF

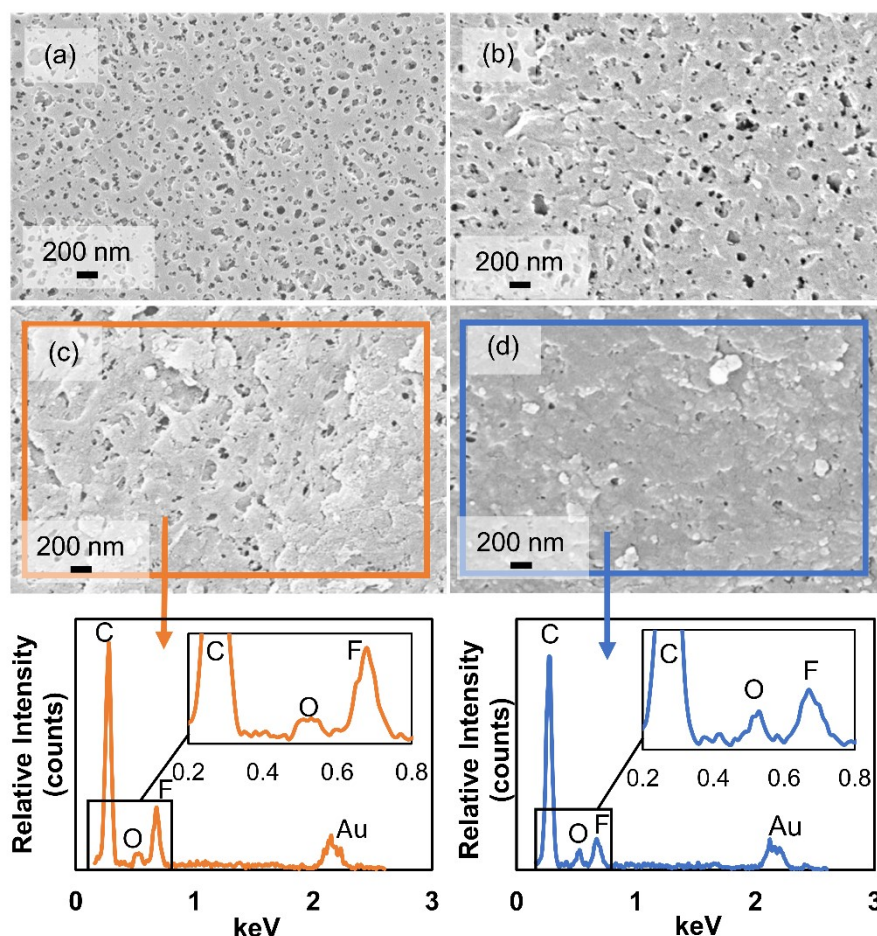


Figure 6.4. SEM images of the separation side surfaces of (a) PVDF_0mins, (b) PVDF_2hrs, (c) PVDF_12hrs, and (d) PVDF_24hrs along with the EDX spectra for (c) PVDF_12hrs in orange and (d) PVDF_24hrs in blue

SEM images of the PDA-modified sample can then be used to gain an understanding of the PDA deposition process and how this affects the membrane surface porosity. The separation side surface images of PDA-modified samples, which are presented in Figure 6.4, suggest that with an increase in immersion time, there is a decrease in the membrane surface porosity as a result of an increase in surface coverage and thickness of the deposited PDA layer. The deposition process first starts by covering the smaller pore sizes, as can be seen for PVDF_2hrs (Figure 6.4b). This is then followed by a reduction in the size of larger pores, as can be seen for PVDF_12hrs (Figure 6.4c). Meanwhile, for the PVDF_24hrs sample, it can be seen that almost the entire surface is covered with PDA (Figure 6.4d). Similar trends were also observed in other such studies reported in the literature [89-94].

Table 6.1 then presents the mean flow pore size and the through-pore membrane porosity as analysed by liquid-liquid displacement porometry (LLDP) for PVDF_0mins sample. The corresponding pore size distribution is also shown in Figure 6.5. Since PVDF_0mins is an unmodified hydrophobic PVDF CCD membrane prepared using 20wt.% polymer dope, its pore characteristics match with those reported in our earlier study presented in section 5.3.2 [88].

Table 6.1. Pore characteristics of PVDF_0mins sample

Pore characteristics	Value
Mean flow pore size	33 ± 2 nm
Through-pore membrane porosity φ_{poro}	12 ± 1 %

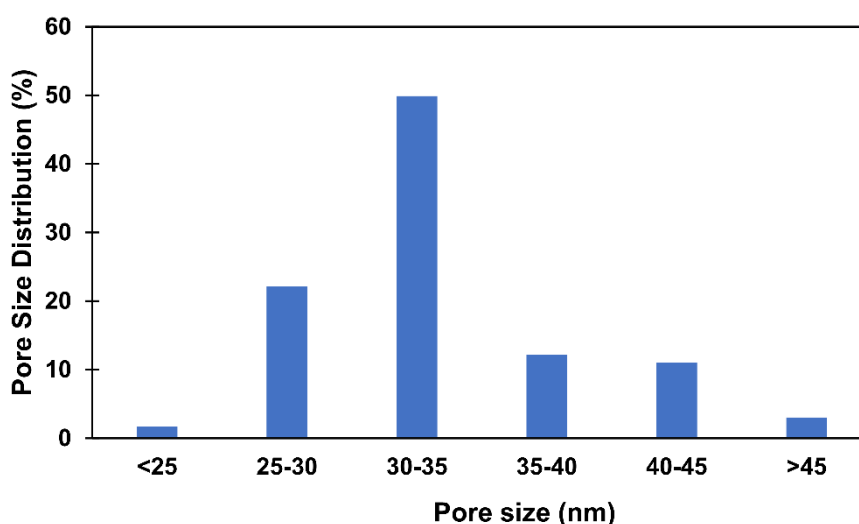


Figure 6.5. Pore size distribution of PVDF_0mins sample

For the PDA-modified samples, it was not possible to measure the pore characteristics using the LLDP method. This was because LLDP as a method relies on the capillary pressure experienced by the wetting and pushing liquids as it permeates through the pore wall. With PDA deposition, the interfacial tension between the solid pore wall and the two liquid changes which unavoidably affects the capillary pressure [95]. The extent to which the interfacial tension changes as a result of PDA deposition cannot be accounted for, which ultimately results

in an inaccurate estimation of the membrane pore sizes. Appendix D provides additional details in this regard.

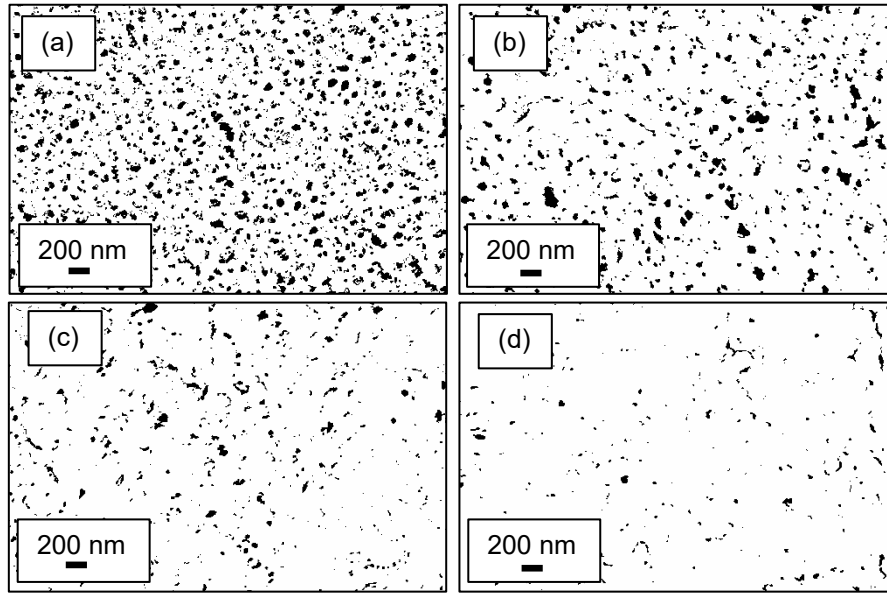


Figure 6.6. Processed SEM images after thresholding of the separation surfaces of (a) PVDF_0mins, (b) PVDF_2hrs, (c) PVDF_12hrs and (d) PVDF_24hrs

To compensate for the lack of quantitative pore characteristics data for the PDA-modified samples, SEM micrographs of the separation surfaces were then processed via image thresholding to compute the surface porosity values ϕ_{SEM} . The level of thresholding was visually adjusted and so is subject to a slight variation in the analysis due to human error. Figure 6.6 provides the processed images after thresholding, while the surface porosity values computed after analysis are summarised in Table 6.2. In line with the SEM images, the result in Table 6.2 also clearly suggest that an increase in immersion time results in a reduction in the surface porosity ϕ_{SEM} . On comparing the ϕ_{SEM} to the ϕ for PVDF_0mins, the latter is smaller than the former. This is because the evaluation of ϕ_{SEM} relies solely on the surface morphology and hence fails to distinguish between through-pores and dead-pores. The evaluation of ϕ on the other hand, only considers those through-pores which contribute to flow, and hence it would give a more reliable estimation of the membrane porosity. Although it was not possible to measure ϕ for the PDA-modified samples, its trend would closely follow that of ϕ_{SEM} . Similarly with regards to the mean flow pore sizes for the modified samples, from the SEM

images, it can safely be assumed that the pore sizes would be $\leq 33\text{nm}$ as a result of PDA deposition.

Table 6.2. Surface porosity for PDA modified samples analysed by using ImageJ software using image threshold enhancement of separation side SEM images

Sample ID	Surface porosity φ_{SEM} (%)
PVDF_0mins	14.6
PVDF_2hrs	8.5
PVDF_12hrs	4.3
PVDF_24hrs	1.6

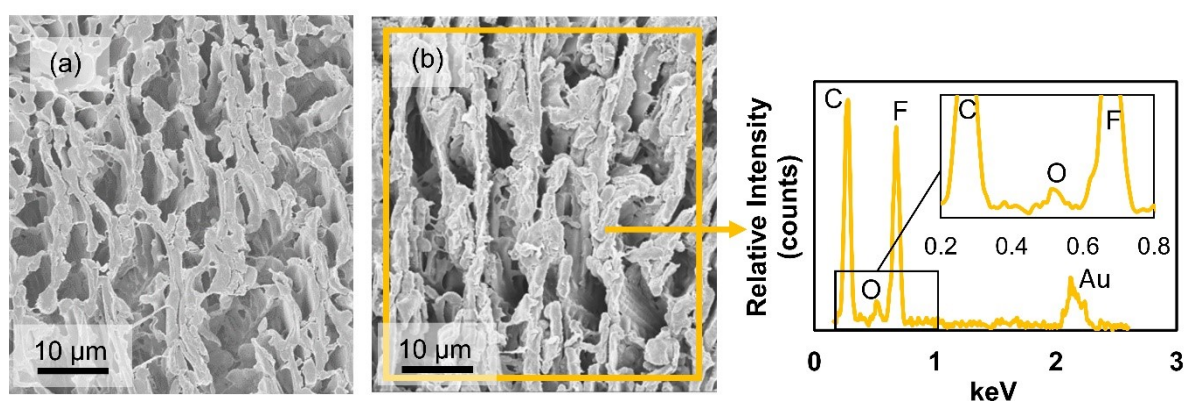


Figure 6.7. SEM images of the support side surfaces of (a) PVDF_0mins and (b) PVDF_24hrs with its EDX spectra in yellow

With regards to the support surfaces, which also get functionalised, there is almost no change in the surface morphology as a consequence of PDA deposition. Figure 6.7 presents the support side surface images of PVDF_0mins and PVDF_24hrs, the representative samples of the two extreme conditions. For the PVDF_24hrs sample, the morphology of the support surface is in wide contrast to the morphology of its separation surface. While almost all of its pores on the separation side were blocked away by the PDA layer, the pores on the support side still resemble very much like that of pure PVDF sample i.e. PVDF_0mins. Since PVDF_24hrs is the sample with the longest immersion time, it would be safe to assume that the support surfaces of other samples with relatively shorter immersion time would also be closely similar to that of PVDF_0mins. Similarly, the membrane cross-sections for both the

samples as shown in Figure 6.8 also look very similar, with a dense separation layer and a support layer composed of interconnected microchannels, a characteristic feature of CCD membranes. Thus it can be concluded from the SEM images that although PDA deposition significantly affects the separation surface morphology and porosity, the support surface morphology along with the characteristic CCD microchannel structure in the membrane cross-section is still retained.

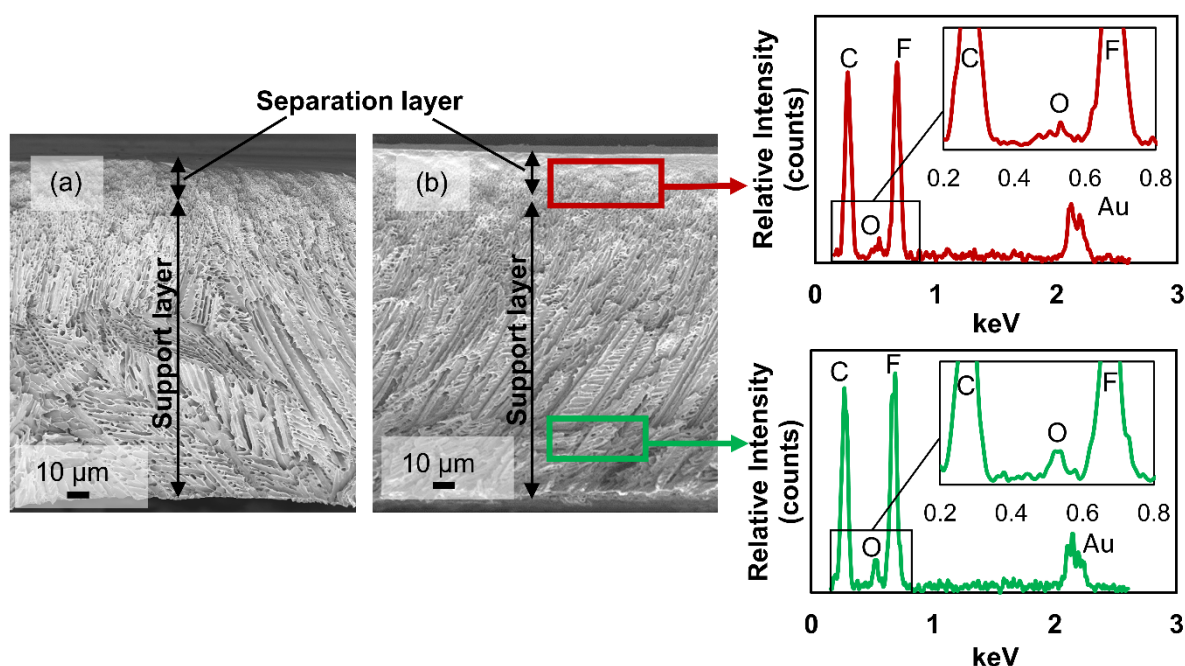


Figure 6.8. SEM images of the membrane cross-sections of (a) PVDF_0mins and (b) PVDF_24hrs with EDX spectra analysed at the top separation layer (red) and the bottom support layer (green)

The elemental mapping was then used to analyse the distribution of the PDA across the membranes. The EDX spectra detect the presence of four elements: carbon, fluorine, oxygen and gold. Carbon being the building block of all organic compounds is detected here owing to the presence of both PVDF and PDA. However, fluorine and oxygen exclusively indicate the presence of PVDF (containing CF_2 units) and PDA (containing hydroxyl $-\text{OH}$ groups), respectively. Thus the oxygen to fluorine (O to F) ratio, by atomic composition, indicates the relative presence of PDA to PVDF in the analysed sample. In addition to hydroxyl (OH) groups, PDA also has amine groups (NH) in its structure. However, the nitrogen signal does not show up in the EDX spectra. This could be caused by the lower elemental presence of

nitrogen compared to oxygen in the suggested molecular structures for polydopamine [73]. As a result, the EDX resolution may not be high enough to detect the presence of nitrogen [96]. Lastly, the gold signal comes from the coating that was done on the samples prior to SEM and hence was excluded from the atomic composition analysis. Table 6.3 compares the atomic composition of various samples computed from their EDX spectra.

Table 6.3. Atomic composition determined by the EDX detector for various SEM samples

Sample ID	Carbon (C)	Oxygen (O)	Fluorine (F)	O to F
PVDF_12 hrs separation surface	77.10%	4.60%	18.30%	0.25
PVDF_24 hrs separation surface	83.5%	6.2%	10.2%	0.61
PVDF_24 hrs support surface	57.6%	4%	38%	0.11
PVDF_24 hrs cross section-top separation layer	52.8%	2.6%	44.6%	0.06
PVDF_24 hrs cross section-bottom support layer	50.5%	5.2%	44.3%	0.12

The separation surfaces (Figure 6.4) were analysed for their EDX spectra to understand the effects of immersion time on the concentration of the deposited PDA. The analysis was limited to just the two samples with the longest modification times (i.e. PVDF_12hrs and PVDF_24hrs) to ensure a clear detection of the relatively shorter oxygen signal can be obtained. From the EDX spectra in Figure 6.4, the signal height of oxygen relative to fluorine is higher for PVDF_24hrs than it is for PVDF_12hrs. In line with the spectra, Table 6.3 also shows that the O to F ratio, which indicates the relative presence of PDA to PVDF, is much higher for the former sample than it is for the latter. This suggests a successful increase in surface coverage of hydrophobic PVDF by the hydrophilic PDA with an increase in the immersion time, just as the SEM images indicated by the change in surface morphology.

EDX spectra were also obtained from the support-side surface (Figure 6.7) and the top and bottom parts of the membrane cross-section of PVDF_24hrs sample (Figure 6.8). This was done to gain an understanding of the dopamine penetration process as it occurs from both sides

of the membrane and hence also functionalises the inside structure of the membrane. The oxygen signal being detected on the support surface of PVDF_24hrs (Figure 6.7), indicates successful PDA deposition on this side of the membrane too. However, the O to F ratio is considerably higher in the separation surface than it is in the support surface as can be seen in Table 6.3. This suggests that the PDA layer covering the support side may not be as dense as it is on the separation side as the larger sized micropores on the support surface would allow for easy penetration of the dopamine solution. Despite the very high O to F ratio found on the separation surface, the layer (top separation layer shown in red in Figure 6.8) just underneath it in the membrane cross-section, has a significantly lower O to F ratio (Table 6.3). This further suggests that the PDA penetration would indeed be inhibited from the separation side. On the other hand, the EDX spectra of the bottom support layer (shown in green in Figure 6.8), shows an almost identical O to F ratio (Table 6.3) to that of the support surface. This suggests effective dopamine solution penetration from the support side along with successful functionalisation of the CCD microchannels.

From the above findings, a PDA modification process on the CCD membrane can be summarised through an illustration which is presented in Figure 6.9. At shorter immersion times, mean flow pore sizes of the membrane (around 30 nm) along with its overall cross-section morphology are retained while still having some degree of successful PDA deposition. However, at longer immersion times, the PDA penetration inside the membrane cross-section from the separation side is largely inhibited resulting in a thick and dense PDA layer being deposited on the separation surface itself. This results in smaller mean flow pore sizes and contributes to a reduction in the overall surface porosity. In contrast to the separation surface, the support surface behaves more like an MF membrane, where the pore sizes are much larger than the penetrating PDA molecules [92]. As a result, without blocking any pores, this support side of the membrane facilitates effective functionalisation of the interconnected microchannels found in the CCD membranes. It is this feature that sets CCD membranes apart from the typical NIPS membranes [2, 74-78]. NIPS membranes have a tight skin-like separation layer and a sponge-like disconnected morphology in the support layer [97]. Thus, the PDA penetration would be indeed be inhibited from both sides of the NIPS membrane, which in turn would limit the functionalisation of its inside cross-section [2, 74-78]. The effective functionalisation of the microchannels present in the CCD membrane's cross-section would help in improving the overall anti-fouling performance of the membrane as it would

inhibit the adhesion of any small-sized foulants that may have found their way in from the separation side during a filtration process.

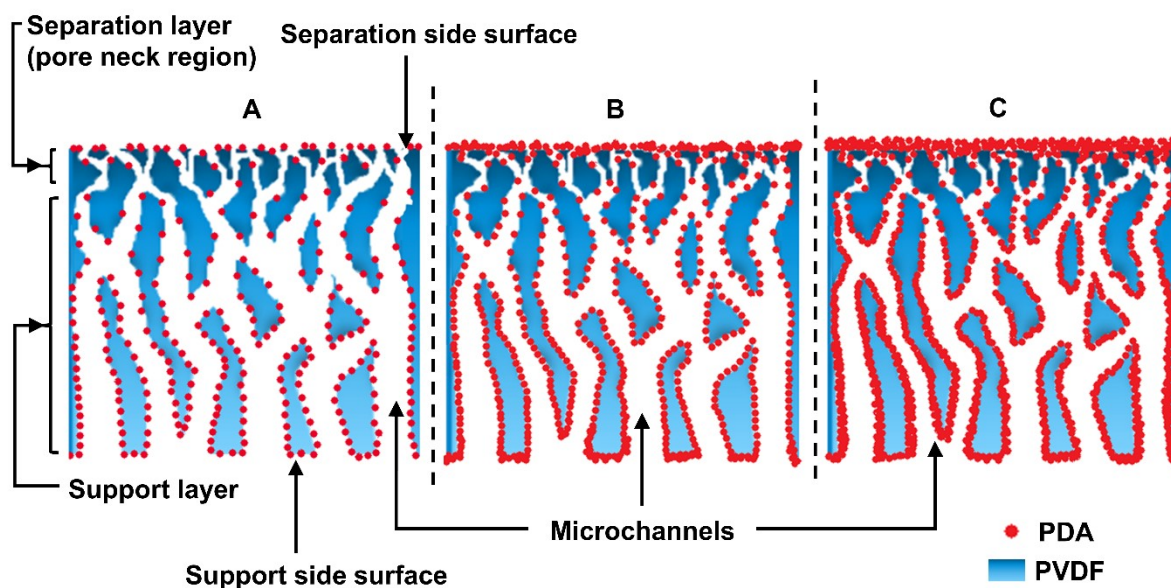


Figure 6.9. Illustration of the PDA modification process that occurs on the CCD membranes with an increase in immersion time (PDA molecules are shown as red dots)

The effect of PDA deposition on the surface porosity can also be deduced from the PWP results. Figure 6.10 shows the PWP values (in blue) for various PDA modified samples. As can be seen from the result, up until an hour of immersion in the dopamine solution, the PWP of the modified membranes remains closely similar to that of pristine PVDF. This suggests that the surface porosities remain fairly unchanged in samples that are modified for shorter durations. At longer modification times (>2 hrs) however, there is a considerable reduction in the PWP, which suggests a substantial increase in the resistance to flow. This would therefore be the result of increased pore-blockages and reduced surface porosities in samples that are modified for such long durations.

Along with pure water permeances, Figure 6.10 also presents the WCA results (in red) for various PDA-modified samples. As expected, the general trend is similar to that of PWPs. The WCA of PVDF_0mins is measured to be around $88 \pm 2^\circ$. With an increase in immersion time, the WCA decreases and thus suggests a successful increase in the membrane surface hydrophilicity. However, upon closer inspection, it can also be seen that a plateauing trend is observed for WCAs between the immersion time of 2 hrs and 8 hrs, before another substantial

reduction occurs. This suggests that after an initial increase in surface hydrophilicity, once a good surface coverage has been established, the effect of increasing PDA deposition to further increase the surface energy is offset by the effect of pore-blocking (as evidenced by SEM and PWP). When the membrane pores are blocked, the membrane surface roughness also decreases. As a result, there is no further decrease in the apparent WCAs between 2hrs and 8 hrs, as it is well known that membrane porosity and surface roughness can also significantly influence the observed WCAs [98]. Once the immersion time is further increased beyond this point (12 to 24 hrs), the surface energy once again dominates resulting in further reduced contact angles to as low as $42 \pm 3^\circ$ for PVDF_24hrs sample. Similar drops in contact angles have also been reported in other studies that have used PDA to modify the surface of PVDF [76, 99].

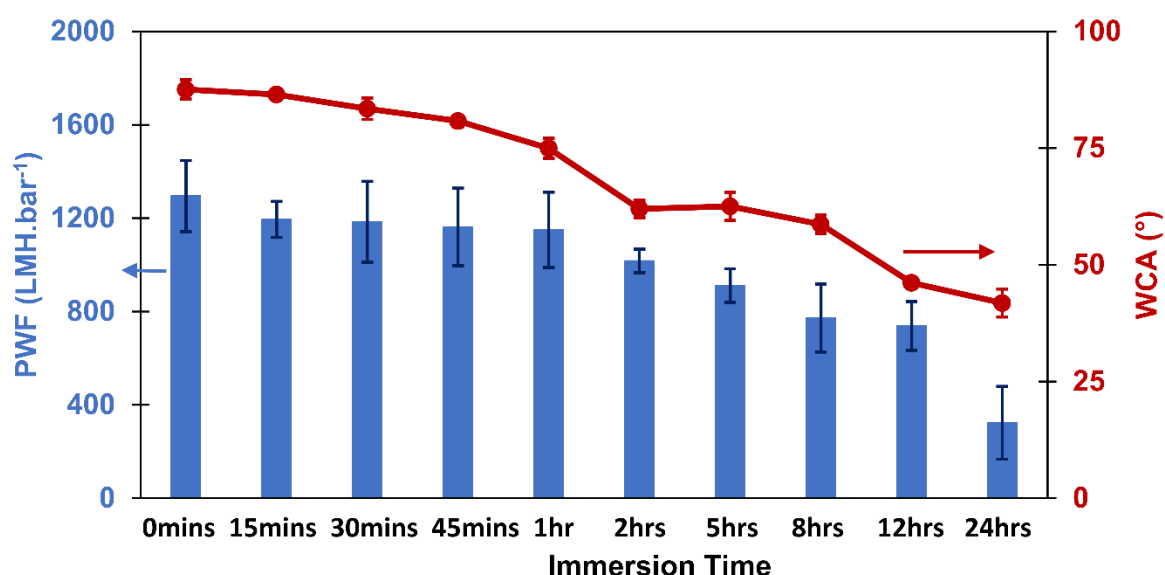


Figure 6.10. PWPs and WCAs measured for the PVDF samples modified with PDA for varying immersion times

6.3.2 BSA Fouling Study

From the previous section, it can be inferred that a trade-off does exist during the modification process. On one hand, PDA deposition improves the surface hydrophilicity, but on the other, it also reduces the surface porosity. While the former helps in reducing the membrane fouling tendency, the latter results in a reduced PWP. As a result, a balance must be sought between the two counter opposing properties to optimise the overall permeation performance. To achieve this, fouling studies on the modified membranes were performed.

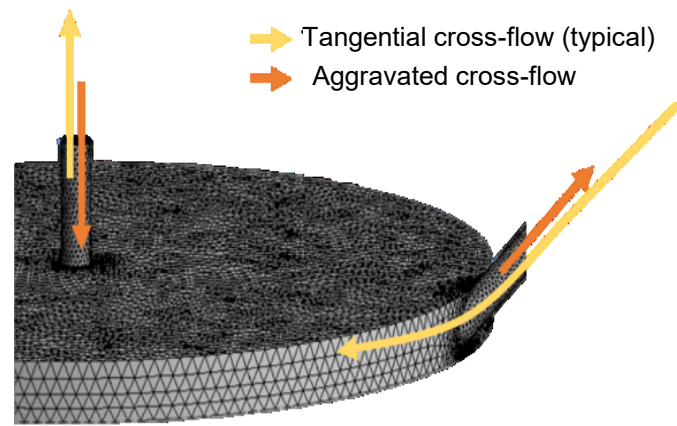


Figure 6.11. Illustration of two different cross-flow setups

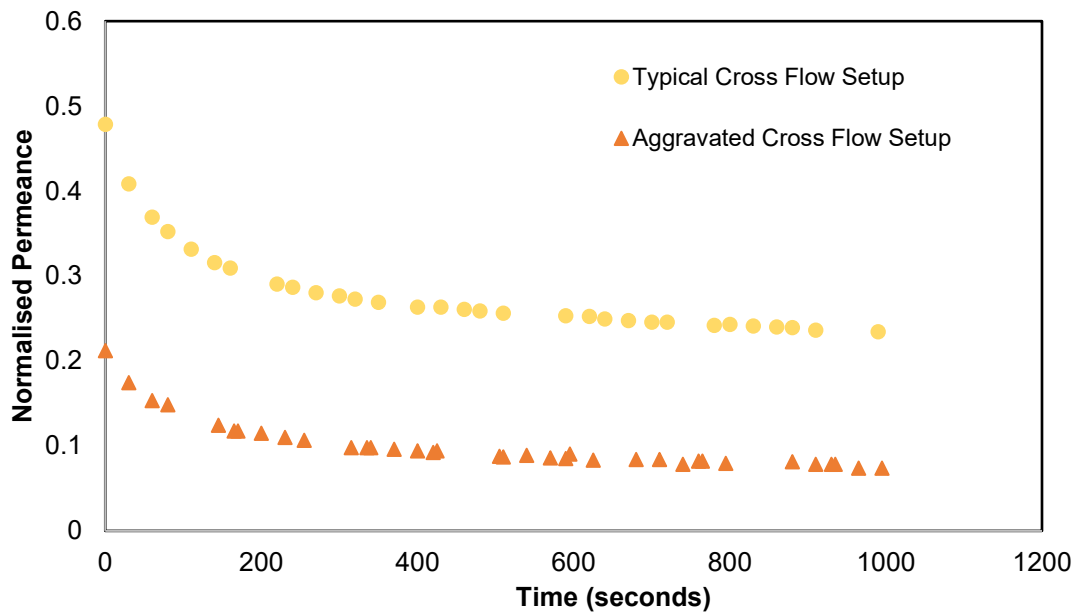


Figure 6.12. Normalised permeance trend of the permeate during the BSA filtration on PVDF_0mins sample when tested under different cross-flow setups.

Before commencing the fouling study, two different cross-flow configurations were investigated: tangential (normal) and aggravated configurations. The illustrations for both these configurations are given in Figure 6.11. The purpose of this study was to investigate which configuration would give a worse fouling condition with a BSA feed stream on PVDF_0mins sample. The result, presented in Figure 6.12, shows that the membrane sample suffers a more serious permeance decline (by over three times) in the aggravated configuration than in the normal one. In the normal cross-flow set up, there is a tangential orientation of the feed inlet which results in a swirling flow towards the centre. Meanwhile, the aggravated cross-flow set

up resembles more like a dead-end filtration that accelerates the membrane fouling. Therefore, since the purpose of this study was to investigate the membranes' behaviour in the worst-case fouling scenario, the aggravated cross-flow setup was then chosen. It should be noted however that in practice tangential cross-flow setup would be used and hence the permeance decline and fouling tendencies would not be as severe.

PDA-modified PVDF samples with immersion times of 0, 2, 12 and 24 hrs were then chosen for this study to evaluate the effectiveness of PDA deposition in improving the anti-fouling capabilities. The samples were chosen to represent the pristine membrane and membranes that were modified for short, intermediate and long durations, respectively. The result for the water permeance for these membranes during the fouling test is then given in Figure 6.13.

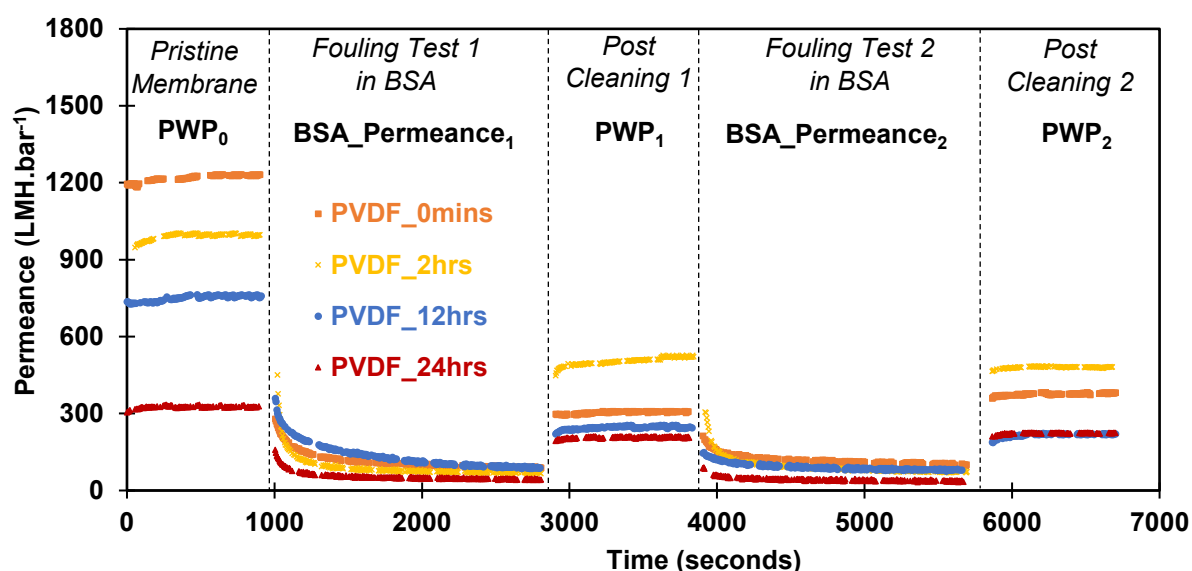


Figure 6.13. Variation in permeance with time for various PVDF samples in either pure water or BSA fouling environment

From Figure 6.13, it can be seen that the pure water permeance of the pristine membranes before BSA exposure (PWP_0) follows a similar trend as previously observed in Figure 6.10. The PWP_0 is lower for samples with longer exposure to the dopamine solution because of the increased pore blockage by the deposited PDA. Upon exposure to the BSA feed in the first fouling cycle, all of the membranes suffer a decline in permeance before reaching a plateau at around 45-90 $LMH.bar^{-1}$. The decline in permeance is the result of membrane fouling

combined with the concentration polarisation effects, all of which are exacerbated in this aggravated dead-end type cross-flow setup.

After this period, all the membranes were then cleaned and their pure water permeances (PWP_1) then measured. From the result, it can be seen that the trend for the PWP_1 , as measured for various samples, no longer follows the initial trend for PWP_0 . In this case, PVDF_2hrs gives the highest water permeance followed by PVDF_0mins, PVDF_12hrs and PVDF_24 hrs in descending order. All of the membranes were then again exposed to the BSA feed in the second fouling test. Just as it was observed in the previous cycle, all of the membranes suffer a similar decline in permeance after which they plateau around 35-100 LMH.bar⁻¹. The process of cleaning the membranes and measuring their pure water permeances (PWP_2) was then repeated just as before. The trend for PWP_2 follows the same trend as it was for PWP_1 , with PVDF_2hrs sample still having the highest water permeance. This then signals the initial advantage of modifying the PVDF membrane with the PDA layer.

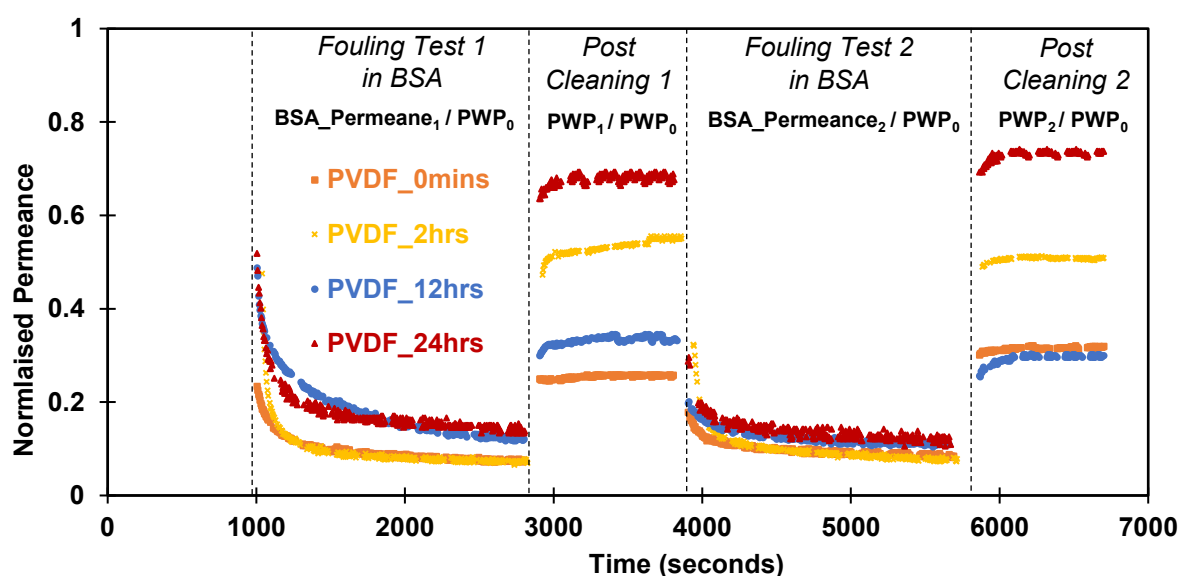


Figure 6.14. Variation in normalised permeance with time for various PVDF samples either pure water or BSA fouling environment

To get a clearer picture of the membrane performance and permeance recovery, the permeances for all the samples were normalised against their corresponding PWP_0 values and presented in Figure 6.14. As can be seen in Figure 6.14, the permeance decline for PVDF_0mins and PVDF_2hrs is very fast compared to PVDF_12hrs and PVDF_24hrs. This suggests a better fouling resistance in samples treated with PDA for longer times. However, all

samples, in general, show a considerable decline in permeance. Many times, the decline in permeance could be merely due to concentration polarisation and not due to irreversible fouling by adsorption on the membrane [100, 101]. Moreover, because of the aggravated cross-flow set up, the effects of fouling and concentration polarisation are more pronounced than they would have been in a tangential cross-flow set up which is typically used during commercial filtration processes. Thus it is important to distinguish between reversible and irreversible fouling as the former can be minimised in practice during filtration applications by regular cleaning, increasing the turbulence (by increasing flowrate or using specialised feed spacers), or using tangential cross-flows to limit the effects of concentration polarisation.

The reversible and irreversible fouling factors and the permeance recovery ratios were then computed with the result presented in Figure 6.15. From Figure 6.15, it can be seen that PVDF_24hrs has the lowest irreversible fouling factor F_{ir} (average of 0.33) and the highest PRR (0.67). With an increase in PDA deposition time, although the absolute values of PWP_0 decreases, the increased surface hydrophilicity limits the adsorption of BSA onto the membrane surface, which results in better flux recoveries post fouling. Whilst this effect was true for PVDF_2hrs and even more so for PVDF_24hrs, PVDF_12hrs was an outlier. The PRRs and F_{ir} of PVDF_12hrs were very similar to that of PVDF_0 hrs. It must also be mentioned that the PRRs and the fouling factors remain similar between the two cycles which suggest that they have reached their steady-state critical values.

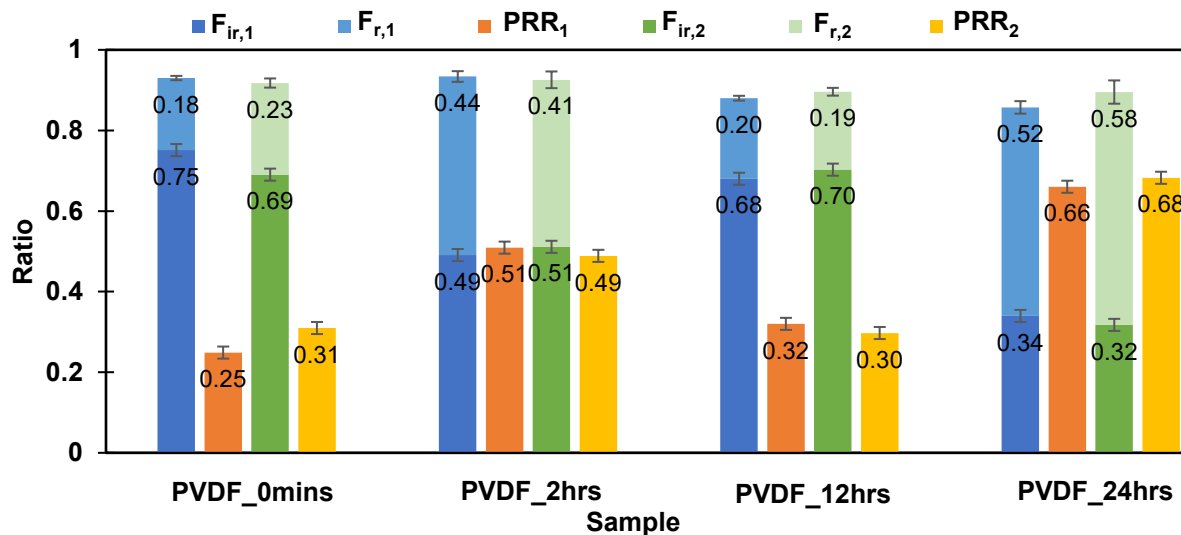


Figure 6.15. Irreversible (F_{ir}) and Reversible (F_r) fouling factors for fouling cycle 1 and 2 along with the corresponding permeance recovery ratios (PRRs)

The variation in fouling phenomena as experienced by membranes' separation layers that are either non-modified or modified for short (2hrs), intermediate (12hrs) and long (24hrs) duration times is illustrated in Figure 6.16. The poor PRR and high F_{ir} of PVDF_0mins can be attributed to membrane fouling as a result of the adsorption of BSA molecules onto the membrane surface and pore walls. Meanwhile, given the high surface hydrophilicity of PVDF_12hrs (as evidenced by WCAs), the adsorption of BSA onto the membrane surface should be relatively low. The poor PRR of PVDF_12hrs can then be attributed to the entrapment of BSA molecules inside the pores as opposed to its adsorption on the surface. BSA molecules are reported to have an ellipsoidal dimension of 14nm x 4 nm x 4nm [102-104]. Therefore, given the aspect ratio of BSA molecules, it would be very easy for them to penetrate the pores of pristine PVDF CCD UF membranes (i.e. PVDF_0mins) with nominal pore sizes of around 30 nm [86, 88]. In water, it is possible that the BSA molecules fold inwards, but nevertheless the small dimensions may allow them to penetrate through the membrane pores with relative ease. With an increase in the PDA deposition time, SEM results showed that there was a reduction in surface porosity and pore sizes. Although it was not possible to measure the exact pore sizes for different samples, it should follow this trend where pore sizes of PVDF_0mins > PVDF_2hrs > PVDF_12hrs > PVDF_24hrs. Post completion of a BSA fouling cycle, the membranes are cleaned in an ultrasonic bath for 30 mins to remove any loosely bound BSA molecules. While BSA may have been able to enter the membrane cross-section of PVDF_12hrs given its ellipsoidal dimension, it may have been entrapped inside the membrane cross-section unable to be removed out by ultrasonic cleaning resulting in a poorer PRR. By comparison, although PVDF_2hrs was not as hydrophilic as PVDF_12hrs, the former does have a relatively larger pore size than the latter. This would then allow the loosely bound BSA to be removed out of the membrane cross-section easily by ultrasonic cleaning in the former than the latter. PVDF_24hrs which has even smaller pore sizes and better hydrophilicity would repel most of the BSA molecules at the surface itself and hence eliminate any possibility of BSA penetration. This was then confirmed by analysing the BSA rejection performance for all the membranes, the result of which is presented in Figure 6.17. From the result, it can be seen that the BSA rejection increases with a longer PDA deposition time on the membrane. It is also another indication of a reduction in membrane pore sizes as was seen from SEM results. The improvement in membrane surface hydrophilicity combined with the reduced pore sizes would thereby limit the BSA adsorption and penetration into the membrane pore. The reason for higher rejections in fouling cycle 2 (R_2) than in cycle 1 (R_1) is because the fouled membrane

already had pre-adsorbed or clogged BSA on the surface and pore channels, which would further restrict the permeation of new incoming BSA across the membrane cross-section.

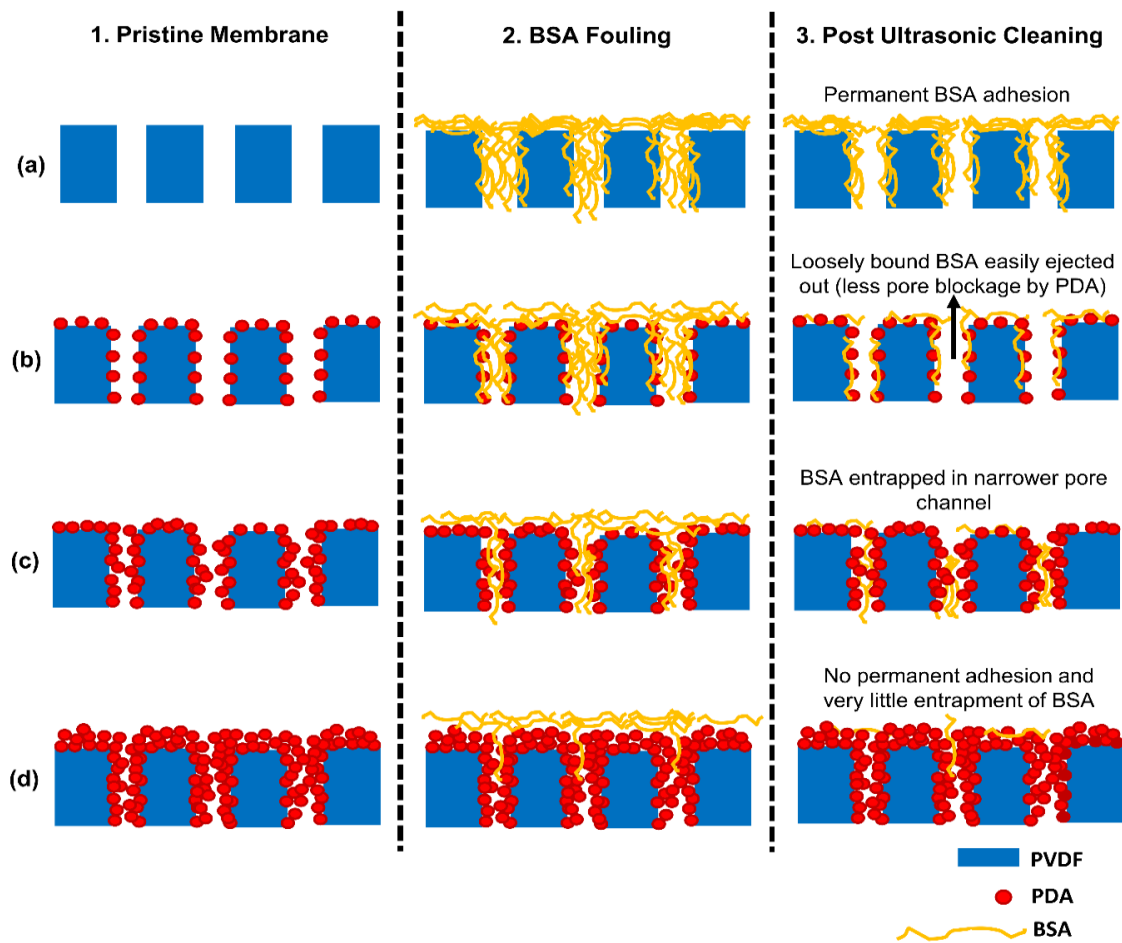


Figure 6.16. BSA fouling phenomena as experienced by the separation layer of (a) PVDF_0mins, (b) PVDF_2hrs, (c) PVDF_12hrs and (d) PVDF_24hrs

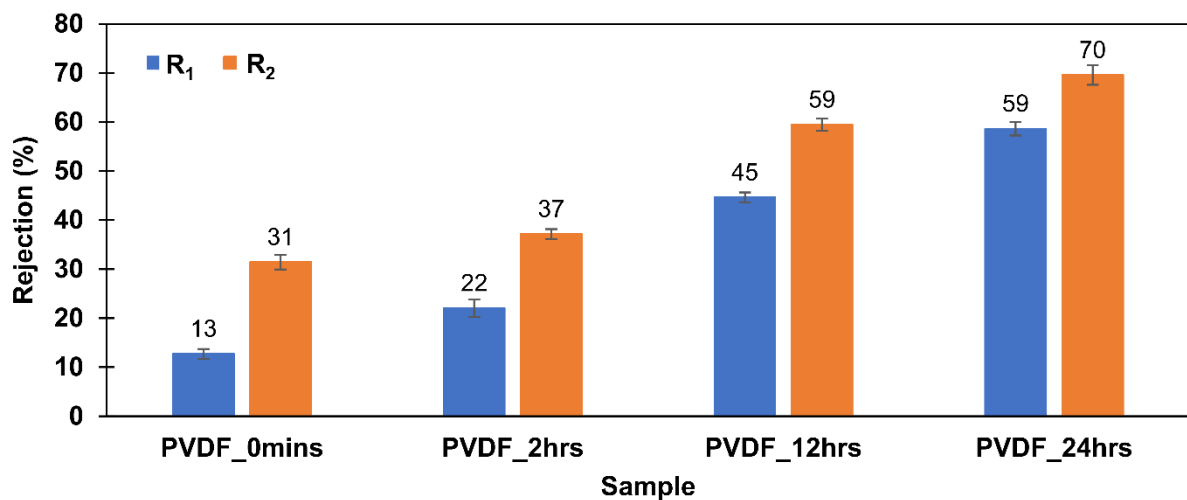


Figure 6.17. BSA rejections for fouling cycle 1 and 2 computed for various samples

From the above analysis, it can be concluded that PVDF_24hrs has the best fouling recovery as high as about 67%. However, its absolute post-fouling water permeance values are still lower than that of PVDF_0mins and PVDF_2hrs. This is because its initial PWP itself is as low as 300 LMH.bar⁻¹ compared to 1300 LMH.bar⁻¹ and 1000 LMH.bar⁻¹ for PVDF_0mins and PVDF_2hrs respectively. Thus, it may seem that increasing the modification time may have a counterproductive effect on the overall permeation performance. Despite this, the high fouling recoveries may make PVDF_24hrs suitable for more demanding applications where membranes with smaller pore sizes and tighter separation capabilities may be needed. PVDF_2hrs on the other hand, which did not have as high a fouling recovery as PVDF_24hrs, seems to have the best overall permeation performance with PWPs still as high as 500 LMH.bar⁻¹ even after two cycles of aggravated fouling. The short modification time seems to be the best choice, as it helps improve the membrane surface hydrophilicity to a reasonable extent without having to significantly compromise its surface porosity. The functionalisation of the support layer's microchannels in addition to the separation surface may have also contributed towards reducing the overall adhesion of BSA foulant in the membrane cross-section.

Table 6.4. PWP of commercial PVDF UF membranes with pore sizes in the range of 20-100 nm*

Manufacturer	Brand	Pore size (nm)	PWP (LMH.bar⁻¹)
Dow-Dupont	IntegraPac	30	40-90
	IntegraFlux	30	40-110
Suez	ZeeWeed 1000	20	61-122
	ZeeWeed 1500	20	34-135
Hydranautics	HYDRAcap® MAX	80	34-110
KOCH	PURON	30	40-133
Toray	MEMBRAY	80	72-180
QUA	EnviQ	40	24-158

*Obtained from product brochure published by the manufacturers.

To understand how well these PDA-modified PVDF-CCD UF membranes (with pore sizes ≤ 30 nm) fare in performance against their commercial counterparts, PWPs of various commercial UF PVDF membranes with pore sizes around 20-80 nm are compiled in Table 6.4

(reproduced here from the Table 2.3 in section 2.10). As previously mentioned, PVDF_2hrs with an initial PWP of 1000 LMH.bar⁻¹ can still retain around half of its original value at 500 LMH.bar⁻¹ after being subjected to two cycles of aggravated fouling. From the table, it can be seen that the PWP value of this fouled membrane is still more than 3 times higher than the PWP value of most commercial pristine PVDF membranes (≈ 150 LMH.bar⁻¹). This then shows the true potential of PVDF-CCD membranes, and present them as a viable alternative to the well-established industry standards.

6.4 Conclusion

This study implemented the popular PDA modification technique on hydrophobic PVDF CCD UF membranes to ensure good permeation performance and high anti-fouling capabilities can be attained during filtration processes. The results showed that with a longer modification time, there is a considerable improvement in the membrane surface hydrophilicity but also a serious decline in the PWP as an unavoidable consequence of the increased pore blockage on the separation side by the depositing PDA. A modification time of 24 hrs results in reducing the WCA from 88° to 42° but at the expense of its PWP which comes down from 1300 to 300 LMH.bar⁻¹. The EDX results suggested successful functionalisation of not just the surfaces but also the walls of the characteristic CCD microchannels present in the membrane's cross-section.

The fouling study which compared samples modified for short, intermediate and long times, presented a unique case of poor permeance recovery despite good surface hydrophilicity for intermediate immersion time samples, owing to the clogging and entrapment of BSA molecules in the separation layer as opposed to fouling by adsorption on the separation surface. The long immersion time sample, despite having the lowest irreversible fouling factor and the best fouling recovery, had low values of PWP because of its reduced surface porosity. The short immersion time sample provided the best balance between permeance and anti-fouling capability. In fact, even after fouling this sample maintains a PWP value that is over 3 times higher than many of the pristine industry-standard counterparts. This simple modification strategy hence promises to unleash the true potential of CCD membranes for real-life applications.

6.5 References

1. Zeng, K., et al., *Insight into fouling behavior of poly(vinylidene fluoride) (PVDF) hollow fiber membranes caused by dextran with different pore size distributions*. Chinese Journal of Chemical Engineering, 2018. **26**(2): p. 268-277.
2. Ding, W., et al., *Fouling behavior of poly(vinylidene fluoride) (PVDF) ultrafiltration membrane by polyvinyl alcohol (PVA) and chemical cleaning method*. Chinese Journal of Chemical Engineering, 2020. **28**(12): p. 3018-3026.
3. Sadr, S.M.K. and D.P. Saroj, *14 - Membrane technologies for municipal wastewater treatment*, in *Advances in Membrane Technologies for Water Treatment*, A. Basile, A. Cassano, and N.K. Rastogi, Editors. 2015, Woodhead Publishing: Oxford. p. 443-463.
4. Kimura, K., et al., *Irreversible membrane fouling in microfiltration membranes filtering coagulated surface water*. Journal of Membrane Science, 2008. **320**(1): p. 356-362.
5. Liu, F., et al., *Progress in the production and modification of PVDF membranes*. Journal of Membrane Science, 2011. **375**(1-2): p. 1-27.
6. Kang, G.-d. and Y.-m. Cao, *Application and modification of poly(vinylidene fluoride) (PVDF) membranes – A review*. Journal of Membrane Science, 2014. **463**: p. 145-165.
7. Upadhyaya, L., X. Qian, and S. Ranil Wickramasinghe, *Chemical modification of membrane surface—overview*. Current Opinion in Chemical Engineering, 2018. **20**: p. 13-18.
8. Lü, X., et al., *Preparation of PU modified PVDF antifouling membrane and its hydrophilic performance*. Journal of Membrane Science, 2016. **520**: p. 933-940.
9. Hu, N., et al., *Preparation and Characterization of Hydrophilically Modified PVDF Membranes by a Novel Nonsolvent Thermally Induced Phase Separation Method*. Membranes, 2016. **6**(4): p. 47.
10. Nunes, S.P. and K.V. Peinemann, *Ultrafiltration membranes from PVDF/PMMA blends*. Journal of membrane science, 1992. **73**(1): p. 25-35.
11. Uragami, T., Y. Naito, and M. Sugihara, *Studies on synthesis and permeability of special polymer membranes*. Polymer Bulletin, 1981. **4**(10): p. 617-622.
12. Yuan, Z. and X. Dan-Li, *Porous PVDF/TPU blends asymmetric hollow fiber membranes prepared with the use of hydrophilic additive PVP (K30)*. Desalination, 2008. **223**(1-3): p. 438-447.

13. Wang, P., et al., *Synthesis, characterization and anti-fouling properties of poly (ethylene glycol) grafted poly (vinylidene fluoride) copolymer membranes*. Journal of Materials Chemistry, 2001. **11**(3): p. 783-789.
14. Chen, Y., et al., *Poly (vinylidene fluoride) with grafted poly (ethylene glycol) side chains via the RAFT-mediated process and pore size control of the copolymer membranes*. Macromolecules, 2003. **36**(25): p. 9451-9457.
15. Chen, Y. and H. Kim, *Poly (vinylidene fluoride) grafted with 3-trimethoxysilylpropyl methacrylate for silyl functional membranes*. Reactive and Functional Polymers, 2008. **68**(11): p. 1499-1506.
16. Hester, J., S. Olugebefola, and A. Mayes, *Preparation of pH-responsive polymer membranes by self-organization*. Journal of Membrane Science, 2002. **208**(1-2): p. 375-388.
17. Hester, J., et al., *ATRP of amphiphilic graft copolymers based on PVDF and their use as membrane additives*. Macromolecules, 2002. **35**(20): p. 7652-7661.
18. Zhao, Y.-H., et al., *Improving hydrophilicity and protein resistance of poly (vinylidene fluoride) membranes by blending with amphiphilic hyperbranched-star polymer*. Langmuir, 2007. **23**(10): p. 5779-5786.
19. Li, J.-H., et al., *Improved surface property of PVDF membrane with amphiphilic zwitterionic copolymer as membrane additive*. Applied Surface Science, 2012. **258**(17): p. 6398-6405.
20. Ma, W., et al., *Effect of type of poly(ethylene glycol) (PEG) based amphiphilic copolymer on antifouling properties of copolymer/poly(vinylidene fluoride) (PVDF) blend membranes*. Journal of Membrane Science, 2016. **514**: p. 429-439.
21. Chen, F., et al., *Preparation and characterization of amphiphilic copolymer PVDF-g-PMABS and its application in improving hydrophilicity and protein fouling resistance of PVDF membrane*. Applied Surface Science, 2018. **427**: p. 787-797.
22. Zhao, Y.-H., et al., *Improving Hydrophilicity and Protein Resistance of Poly(vinylidene fluoride) Membranes by Blending with Amphiphilic Hyperbranched-Star Polymer*. Langmuir, 2007. **23**(10): p. 5779-5786.
23. Shen, J., et al., *Fabrication and characterization of amphiphilic PVDF copolymer ultrafiltration membrane with high anti-fouling property*. Journal of Membrane Science, 2017. **521**: p. 95-103.

24. Zhao, J., et al., *Hydrophilic and anti-fouling PVDF blend ultrafiltration membranes using polyacryloylmorpholine-based triblock copolymers as amphiphilic modifiers*. Reactive and Functional Polymers, 2019. **139**: p. 92-101.
25. Hashim, N.A., F. Liu, and K. Li, *A simplified method for preparation of hydrophilic PVDF membranes from an amphiphilic graft copolymer*. Journal of Membrane Science, 2009. **345**(1): p. 134-141.
26. Zhang, L., et al., *Synthesis of Well-Defined PVDF-Based Amphiphilic Block Copolymer via Iodine Transfer Polymerization for Antifouling Membrane Application*. Industrial & Engineering Chemistry Research, 2018. **57**(26): p. 8689-8697.
27. Zhao, J., et al., *Comb-shaped amphiphilic triblock copolymers blend PVDF membranes overcome the permeability-selectivity trade-off for protein separation*. Separation and Purification Technology, 2020. **239**: p. 116596.
28. Liu, L., et al., *Amphiphilic PVDF-g-PDMAPMA ultrafiltration membrane with enhanced hydrophilicity and antifouling properties*. Journal of Applied Polymer Science, 2019. **136**(42): p. 48049.
29. Saini, B., et al., *A novel stimuli-responsive and fouling resistant PVDF ultrafiltration membrane prepared by using amphiphilic copolymer of poly(vinylidene fluoride) and Poly(2-N-morpholino)ethyl methacrylate*. Journal of Membrane Science, 2020. **603**: p. 118047.
30. Folgado, E., V. Ladmiral, and M. Semsarilar, *Towards permanent hydrophilic PVDF membranes. Amphiphilic PVDF-b-PEG-b-PVDF triblock copolymer as membrane additive*. European Polymer Journal, 2020. **131**: p. 109708.
31. Hikita, S., et al., *Structure control of hydrophilized PVDF hollow-fiber membranes using amphiphilic copolymers: PMMA-co-P (HEMA-co-MEA)*. Journal of Membrane Science, 2020. **612**: p. 118421.
32. Yan, L., Y.S. Li, and C.B. Xiang, *Preparation of poly(vinylidene fluoride)(pvdf) ultrafiltration membrane modified by nano-sized alumina (Al₂O₃) and its antifouling research*. Polymer, 2005. **46**(18): p. 7701-7706.
33. Lv, J., et al., *Graphene oxide-cellulose nanocrystal (GO-CNC) composite functionalized PVDF membrane with improved antifouling performance in MBR: Behavior and mechanism*. Chemical Engineering Journal, 2018. **352**: p. 765-773.

34. Ayyaru, S., T.T.L. Dinh, and Y.-H. Ahn, *Enhanced antifouling performance of PVDF ultrafiltration membrane by blending zinc oxide with support of graphene oxide nanoparticle*. Chemosphere, 2020. **241**: p. 125068.
35. Yuan, X.-T., et al., *Multifunctional PVDF/CNT/GO mixed matrix membranes for ultrafiltration and fouling detection*. Journal of Hazardous Materials, 2020. **384**: p. 120978.
36. Zhou, R., et al., *Effects of multi-walled carbon nanotubes (MWCNTs) and integrated MWCNTs/SiO₂ nano-additives on PVDF polymeric membranes for vacuum membrane distillation*. Separation and Purification Technology, 2019. **217**: p. 154-163.
37. Yi, X., et al., *Adsorption Mechanism of Oil-in-Water on a TiO₂/Al₂O₃-Polyvinylidene Fluoride (PVDF) Ultrafiltration Membrane*. Langmuir, 2018. **34**(34): p. 9907-9916.
38. Razmgar, K., E. Saljoughi, and S.M. Mousavi, *Preparation and characterization of a novel hydrophilic PVDF/PVA/Al₂O₃ nanocomposite membrane for removal of As(V) from aqueous solutions*. Polymer Composites, 2019. **40**(6): p. 2452-2461.
39. Sun, D., et al., *Preparation and performance of the novel PVDF ultrafiltration membranes blending with PVA modified SiO₂ hydrophilic nanoparticles*. Polymer Engineering & Science, 2019. **59**(S1): p. E412-E421.
40. Li, J., et al., *PVDF/SiO₂-g-CDs blended membrane for fluorescence detection and adsorption of metal ions*. Environmental Technology, 2020: p. 1-14.
41. Zeng, G., et al., *Preparation and characterization of a novel PVDF ultrafiltration membrane by blending with TiO₂-HNTs nanocomposites*. Applied Surface Science, 2016. **371**: p. 624-632.
42. Benhabiles, O., et al., *Preparation and characterization of TiO₂-PVDF/PMMA blend membranes using an alternative non-toxic solvent for UF/MF and photocatalytic application*. Molecules, 2019. **24**(4): p. 724.
43. Du, J.R., et al., *Modification of poly(vinylidene fluoride) ultrafiltration membranes with poly(vinyl alcohol) for fouling control in drinking water treatment*. Water Research, 2009. **43**(18): p. 4559-4568.
44. Boributh, S., A. Chanachai, and R. Jiraratananon, *Modification of PVDF membrane by chitosan solution for reducing protein fouling*. Journal of Membrane Science, 2009. **342**(1): p. 97-104.

45. Venault, A., et al., *Surface self-assembled zwitterionization of poly (vinylidene fluoride) microfiltration membranes via hydrophobic-driven coating for improved blood compatibility*. Journal of Membrane Science, 2014. **454**: p. 253-263.
46. Revanur, R., et al., *Reactive Amphiphilic Graft Copolymer Coatings Applied to Poly(vinylidene fluoride) Ultrafiltration Membranes*. Macromolecules, 2007. **40**(10): p. 3624-3630.
47. Venault, A., et al., *Simultaneous amphiphilic polymer synthesis and membrane functionalization for oil/water separation*. Journal of Membrane Science, 2020. **604**: p. 118069.
48. Susanti, R.F., et al., *A new strategy for ultralow biofouling membranes: uniform and ultrathin hydrophilic coatings using liquid carbon dioxide*. Journal of membrane science, 2013. **440**: p. 88-97.
49. Rahimpour, A., et al., *Preparation and characterization of modified nano-porous PVDF membrane with high antifouling property using UV photo-grafting*. Applied Surface Science, 2009. **255**(16): p. 7455-7461.
50. Yang, L., et al. *Preparation of a hydrophilic PVDF membranes by electron beam induced grafting polymerization of acrylic acid*. in *Advanced Materials Research*. 2013. Trans Tech Publ.
51. Lim, S.J. and I.H. Shin, *Graft copolymerization of GMA and EDMA on PVDF to hydrophilic surface modification by electron beam irradiation*. Nuclear Engineering and Technology, 2020. **52**(2): p. 373-380.
52. Chen, X., et al., *Plasma-induced PAA-ZnO coated PVDF membrane for oily wastewater treatment: Preparation, optimization, and characterization through Taguchi OA design and synchrotron-based X-ray analysis*. Journal of Membrane Science, 2019. **582**: p. 70-82.
53. Lee, X.J., et al., *Surface grafting techniques on the improvement of membrane bioreactor: State-of-the-art advances*. Bioresource Technology, 2018. **269**: p. 489-502.
54. Wang, P., et al., *Plasma-induced immobilization of poly (ethylene glycol) onto poly (vinylidene fluoride) microporous membrane*. Journal of Membrane Science, 2002. **195**(1): p. 103-114.
55. Liang, S., et al., *Highly Hydrophilic Polyvinylidene Fluoride (PVDF) Ultrafiltration Membranes via Postfabrication Grafting of Surface-Tailored Silica Nanoparticles*. ACS Applied Materials & Interfaces, 2013. **5**(14): p. 6694-6703.

56. Correia, D.M., et al., *Surface wettability modification of poly(vinylidene fluoride) and copolymer films and membranes by plasma treatment*. Polymer, 2019. **169**: p. 138-147.
57. Hilal, N., et al., *Atomic force microscopy study of membranes modified by surface grafting of cationic polyelectrolyte*. Desalination, 2005. **184**(1-3): p. 45-55.
58. Hilal, N., et al., *Surface modified polymeric membranes to reduce (bio) fouling: a microbiological study using E. coli*. Desalination, 2004. **167**: p. 293-300.
59. Matyjaszewski, K. and N.V. Tsarevsky, *Nanostructured functional materials prepared by atom transfer radical polymerization*. Nature chemistry, 2009. **1**(4): p. 276-288.
60. Braunecker, W.A. and K. Matyjaszewski, *Controlled/living radical polymerization: Features, developments, and perspectives*. Progress in Polymer Science, 2007. **32**(1): p. 93-146.
61. Ma, N., et al., *Surface grafting of zwitterionic and PEGylated cross-linked polymers toward PVDF membranes with ultralow protein adsorption*. Polymer, 2019. **167**: p. 1-12.
62. Singh, N., et al., *Surface modification of microporous PVDF membranes by ATRP*. Journal of Membrane Science, 2005. **262**(1): p. 81-90.
63. Matyjaszewski, K. and J. Xia, *Atom transfer radical polymerization*. Chemical reviews, 2001. **101**(9): p. 2921-2990.
64. Matyjaszewski, K., *Atom transfer radical polymerization (ATRP): current status and future perspectives*. Macromolecules, 2012. **45**(10): p. 4015-4039.
65. Chiefari, J., et al., *Living free-radical polymerization by reversible addition-fragmentation chain transfer: the RAFT process*. Macromolecules, 1998. **31**(16): p. 5559-5562.
66. Moad, G., E. Rizzardo, and S.H. Thang, *Radical addition-fragmentation chemistry in polymer synthesis*. Polymer, 2008. **49**(5): p. 1079-1131.
67. Barsbay, M., et al., *Nanopore size tuning of polymeric membranes using the RAFT-mediated radical polymerization*. Journal of Membrane Science, 2013. **445**: p. 135-145.
68. Han, M.J., G.N.B. Baroña, and B. Jung, *Effect of surface charge on hydrophilically modified poly (vinylidene fluoride) membrane for microfiltration*. Desalination, 2011. **270**(1-3): p. 76-83.

69. Marbelia, L., et al., *Poly(vinylidene fluoride)-Based Membranes for Microalgae Filtration*. Chemical Engineering & Technology, 2018. **41**(7): p. 1305-1312.
70. Ding, Y.H., M. Floren, and W. Tan, *Mussel-inspired polydopamine for bio-surface functionalization*. Biosurface and Biotribology, 2016. **2**(4): p. 121-136.
71. Lee, H., et al., *Mussel-Inspired Surface Chemistry for Multifunctional Coatings*. Science, 2007. **318**(5849): p. 426.
72. Ryu, J.H., P.B. Messersmith, and H. Lee, *Polydopamine Surface Chemistry: A Decade of Discovery*. ACS Applied Materials & Interfaces, 2018. **10**(9): p. 7523-7540.
73. Liebscher, J., et al., *Structure of Polydopamine: A Never-Ending Story?* Langmuir, 2013. **29**(33): p. 10539-10548.
74. An, Z., et al. *Rapid deposition on polydopamine coated PVDF membranes with enhanced anti-protein and antiantibacterial performance for wastewater treatment*. in *2020 3rd International Conference on Electron Device and Mechanical Engineering (ICEDME)*. 2020.
75. Muchtar, S., et al., *Polydopamine-coated poly(vinylidene fluoride) membranes with high ultraviolet resistance and antifouling properties for a photocatalytic membrane reactor*. Journal of Applied Polymer Science, 2019. **136**(14): p. 47312.
76. Shao, L., et al., *A facile strategy to enhance PVDF ultrafiltration membrane performance via self-polymerized polydopamine followed by hydrolysis of ammonium fluotitanate*. Journal of Membrane Science, 2014. **461**: p. 10-21.
77. Sri Abirami Saraswathi, M., et al., *BSA and humic acid separation from aqueous stream using polydopamine coated PVDF ultrafiltration membranes*. Journal of Environmental Chemical Engineering, 2017. **5**(3): p. 2937-2943.
78. Syawaliah, S., et al., *The influences of polydopamine immersion time on characteristics and performance of polyvinylidene fluoride ultrafiltration membrane*. MATEC Web of Conferences, 2018. **197**: p. 09007.
79. Li, R., et al., *Inkjet printing of dopamine followed by UV light irradiation to modify mussel-inspired PVDF membrane for efficient oil-water separation*. Journal of Membrane Science, 2021. **619**: p. 118790.
80. Zmerli, I., J.-P. Michel, and A. Makky, *Bioinspired polydopamine nanoparticles: synthesis, nanomechanical properties, and efficient PEGylation strategy*. Journal of Materials Chemistry B, 2020. **8**(20): p. 4489-4504.

81. {Najar, N., Adel, M. Gerland, and M. Jouiad, *Porosity-induced relaxation of strains in GaN layers studied by means of micro-indentation and optical spectroscopy*. Journal of Applied Physics, 2012. **111**(9): p. 093513.
82. Maruyama, T., et al., *FT-IR analysis of BSA fouled on ultrafiltration and microfiltration membranes*. Journal of Membrane Science, 2001. **192**(1): p. 201-207.
83. Beyer, M., B. Lohrengel, and L.D. Nghiem, *Membrane fouling and chemical cleaning in water recycling applications*. Desalination, 2010. **250**(3): p. 977-981.
84. Ding, Y., et al., *Effects of protein properties on ultrafiltration membrane fouling performance in water treatment*. Journal of Environmental Sciences, 2019. **77**: p. 273-281.
85. Le-Clech, P., *Protein Fouling Mechanisms*, in *Encyclopedia of Membranes*, E. Drioli and L. Giorno, Editors. 2015, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 1-2.
86. Wang, B., J. Ji, and K. Li, *Crystal nuclei templated nanostructured membranes prepared by solvent crystallization and polymer migration*. Nat Commun, 2016. **7**: p. 12804.
87. Ariono, D., et al., *The effect of polymer concentration on flux stability of polysulfone membrane*. AIP Conference Proceedings, 2017. **1788**(1): p. 030048.
88. Shah, V., B. Wang, and K. Li, *Blending modification to porous polyvinylidene fluoride (PVDF) membranes prepared via combined crystallisation and diffusion (CCD) technique*. Journal of Membrane Science, 2021. **618**: p. 118708.
89. Jiang, J., et al., *Surface characteristics of a self-polymerized dopamine coating deposited on hydrophobic polymer films*. Langmuir, 2011. **27**(23): p. 14180-14187.
90. Lee, H., et al., *Mussel-inspired surface chemistry for multifunctional coatings*. science, 2007. **318**(5849): p. 426-430.
91. Li, B., et al., *Ultrathin and stable active layer of dense composite membrane enabled by poly (dopamine)*. Langmuir, 2009. **25**(13): p. 7368-7374.
92. McCloskey, B.D., et al., *Influence of polydopamine deposition conditions on pure water flux and foulant adhesion resistance of reverse osmosis, ultrafiltration, and microfiltration membranes*. Polymer, 2010. **51**(15): p. 3472-3485.
93. Ou, J., et al., *Microtribological and electrochemical corrosion behaviors of polydopamine coating on APTS-SAM modified Si substrate*. Applied Surface Science, 2009. **256**(3): p. 894-899.

94. Pan, F., et al., *Bioinspired fabrication of high performance composite membranes with ultrathin defect-free skin layer*. Journal of Membrane Science, 2009. **341**(1-2): p. 279-285.
95. Jang, J., Z. Sun, and J.C. Santamarina, *Capillary pressure across a pore throat in the presence of surfactants*. Water Resources Research, 2016. **52**(12): p. 9586-9599.
96. Yu, F., et al., *Experimental and theoretical analysis of polymerization reaction process on the polydopamine membranes and its corrosion protection properties for 304 Stainless Steel*. Journal of Molecular Structure, 2010. **982**(1): p. 152-161.
97. Bottino, A., et al., *The formation of microporous polyvinylidene difluoride membranes by phase separation*. Journal of Membrane Science, 1991. **57**(1): p. 1-20.
98. Wang, J., et al., *Influence of surface roughness on contact angle hysteresis and spreading work*. Colloid and Polymer Science, 2020. **298**(8): p. 1107-1112.
99. Xi, Z.-Y., et al., *A facile method of surface modification for hydrophobic polymer membranes based on the adhesive behavior of poly(DOPA) and poly(dopamine)*. Journal of Membrane Science, 2009. **327**(1): p. 244-253.
100. Field, R., *Fundamentals of Fouling*, in *Membrane Technology*. 2010. p. 1-23.
101. Sablani, S.S., et al., *Concentration polarization in ultrafiltration and reverse osmosis: a critical review*. Desalination, 2001. **141**(3): p. 269-289.
102. Wright, A.K. and M.R. Thompson, *Hydrodynamic structure of bovine serum albumin determined by transient electric birefringence*. Biophysical journal, 1975. **15**(2 Pt 1): p. 137-141.
103. Monash, P. and G. Pugazhenth, *Effect of TiO₂ addition on the fabrication of ceramic membrane supports: A study on the separation of oil droplets and bovine serum albumin (BSA) from its solution*. Desalination, 2011. **279**(1): p. 104-114.
104. Wang, J., et al., *Bovine serum albumin selective integral asymmetric isoporous membrane*. Journal of Membrane Science, 2020. **604**: p. 118074.

7 Conclusions and Recommendations for future work

This work is the first-ever doctoral thesis focused solely on producing high-performance PVDF membranes using the new innovative Combined Crystallisation and Diffusion (CCD) method. The increasing scarcity of accessible drinking water and the role ultrafiltration membranes can play in dealing with this rising challenge was the motivation behind this research work. It is hoped that the work done in developing the CCD method further will play a pivotal role in bringing about a change in the membrane filtration market. PVDF CCD membranes showed significantly higher PWFs, an order of magnitude higher than their NIPS counterparts. The permeation characteristics were further enhanced by the innovative dual-casting technique that was applied to CCD membranes. To reduce the membrane pore sizes of CCD membranes, the PMMA blending approach was found to be an effective way that did not require any alteration in the preparation operating conditions. Combining the dual-casting technique with the blending modification approach enabled the fabrication of membranes with even smaller pore sizes and unaffected water permeances. Finally, the application of PDA modification to CCD membranes improved the overall anti-fouling tendency of the membranes and maintained relatively higher PWFs even after fouling than its commercial counterparts. The learning outcomes from this thesis will provide the critical technical know-how for large scale CCD based PVDF membrane manufacturing with the capability to replace the already matured techniques of NIPS and TIPS so far practised in the industry.

Since the CCD method is still quite new, there are several areas that can still be explored. Some of these are summarised below:

- Investigate the effect of cooling temperature on the produced pore sizes.

So far only the cooling rate has been altered by varying the cooling/casting plate combination, while the cooling temperature of the freezer was always maintained at around -30°C. A systematic study could be carried out by varying the cooling temperature instead.

- Expand the application of CCD to other materials.

To make the CCD method truly universal, its application should not be limited to just PVDF or PES. Other polymers and inorganic materials could also be considered.

- Explore the possibility of fabricating CCD based membranes in hollow fiber and tubular geometries.

The CCD method involves unidirectional freezing of polymer cast film using a solid media. While this was relatively simpler for flat sheet geometries, further effort could be directed towards the expansion of CCD to other geometries as well.

- Use of blending modification to CCD PVDF membranes.

While this work made use of an effective surface modification technique, blending modification to CCD PVDF membranes could also be considered. This is because with the post membrane fabrication modification, there is always a possibility of pore blockage by the modifying agent, which can be avoided in blending modification.

List of Publications

Journal Publications

Shah, V., B. Wang, and K. Li, *Blending modification to porous polyvinylidene fluoride (PVDF) membranes prepared via combined crystallisation and diffusion (CCD) technique*. Journal of Membrane Science, 2021. **618**: p. 118708.

Shah, V., N. Prasetya, and K. Li, *Polydopamine modification of high-performance PVDF ultrafiltration membranes prepared by the Combined Crystallisation and Diffusion (CCD) method*. Journal of Membrane Science, 2021. **635**: p. 119538.

Shah, V., B. Wang, and K. Li, *High-performance PVDF membranes prepared by the Combined Crystallisation and Diffusion (CCD) method using a dual-casting technique: a breakthrough for water treatment applications*. Energy and Environmental Science, 2021 (resubmitted and under review)

Peng, H., V.Shah, and K.Li, *Morphology and performance of Polyvinylidene fluoride (PVDF) membrane prepared by the CCD method: thermodynamic considerations*. Journal of Membrane Science, 2021 (under review)

Conference Publications

Shah, V., B. Wang, and K. Li, *Ultrafiltration membranes prepared by combined crystallisation & diffusion (CCD) technique*. MELPRO, 2018, Prague (oral)

Shah, V., B. Wang, and K. Li, *Combined crystallisation & diffusion (CCD) technique*. NYM, 2018, Valencia (oral)

Shah, V., B. Wang, and K. Li, *Fabrication of ultrafiltration membranes by combined crystallisation & diffusion (CCD) technique*. Euromembrane, 2018, Valencia (oral)

Shah, V., B. Wang, and K. Li, *Ultrafiltration PVDF membranes prepared by combined crystallisation & diffusion (CCD) technique*. AIChE, 2020, Virtual (oral)

Shah, V., B. Wang, and K. Li, *Preparation and Modification of Ultrafiltration Polyvinylidene Fluoride (PVDF) membranes by Combined Crystallisation Diffusion (CCD) technique*. ICOM, 2020, Virtual (oral)

APPENDICES

APPENDIX A – Membrane casting setup

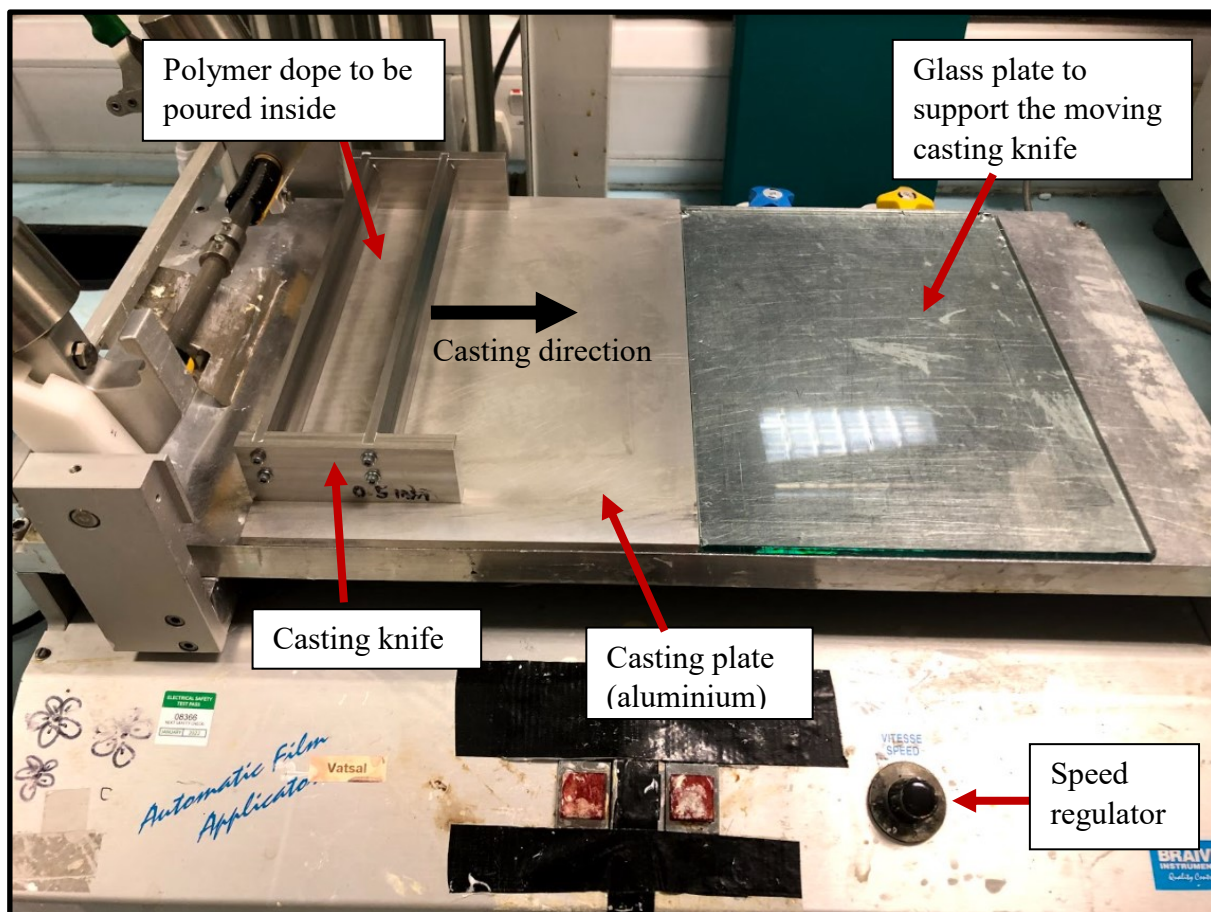


Figure A-1 Membrane casting set-up

APPENDIX B – Membrane Characterisation

B1- Scanning Electron Microscopy (SEM)

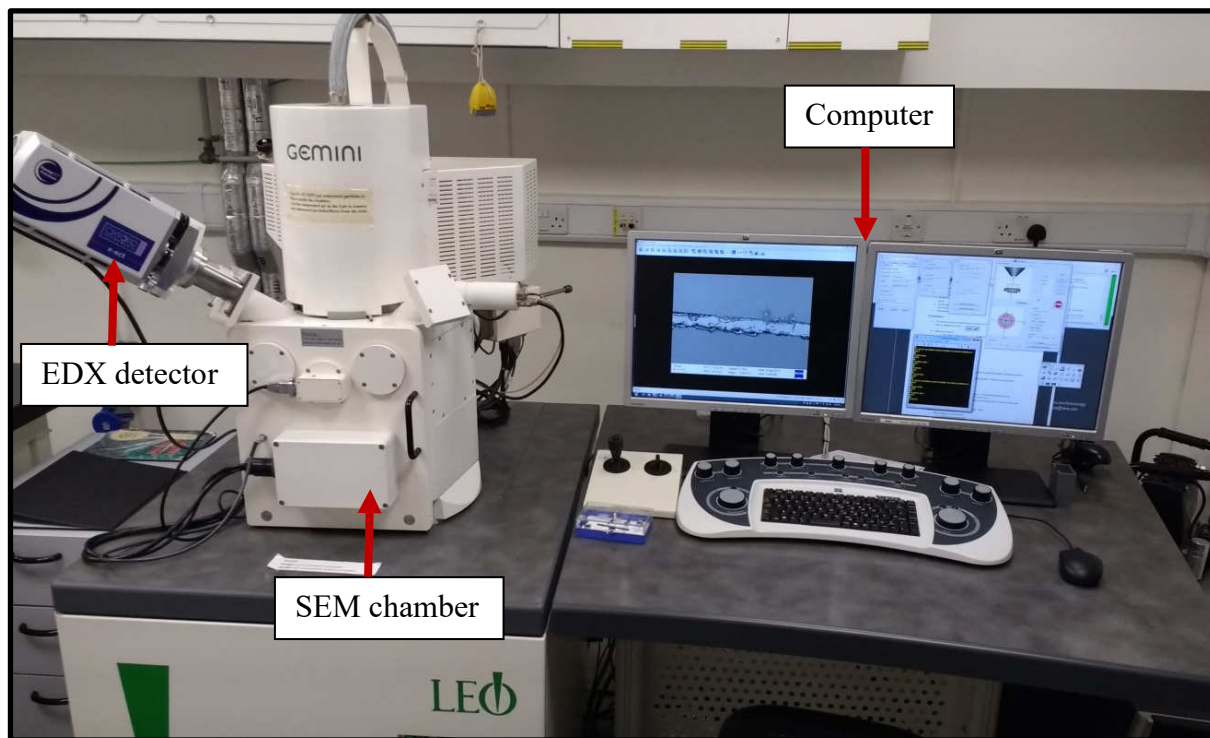


Figure B-1. LEO Gemini 1525 FEGSEM with EDX detector

B2- Mean flow pore sizes and through-pore porosity

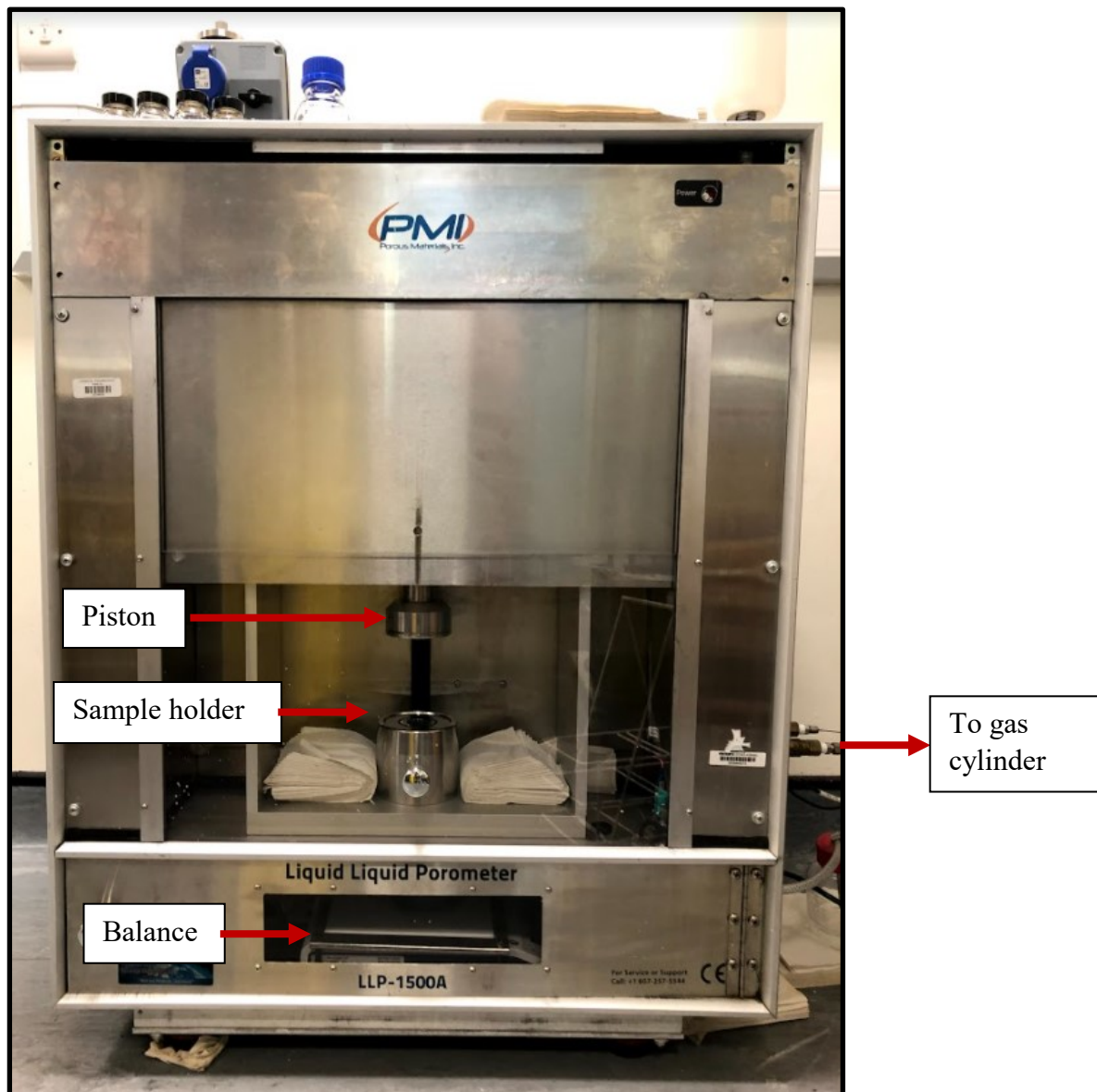


Figure B-2. Liquid-liquid displacement porometer used to measure the mean flow pore size and through-pore membrane porosity

B3- Pure water permeance (PWP)

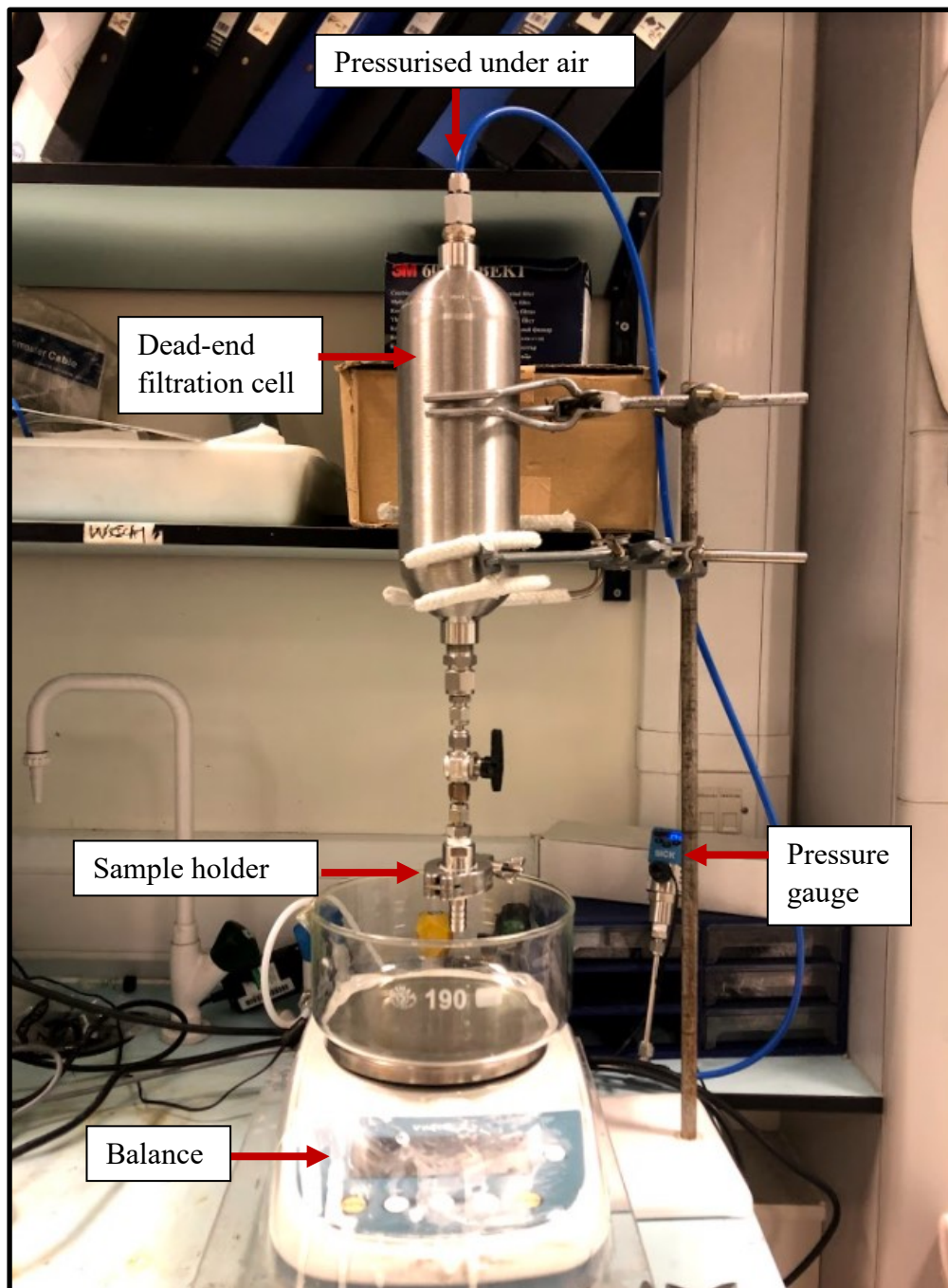


Figure B-3. Dead-end filtration set-up used to measure pure water permeance

B4- Mechanical strengths

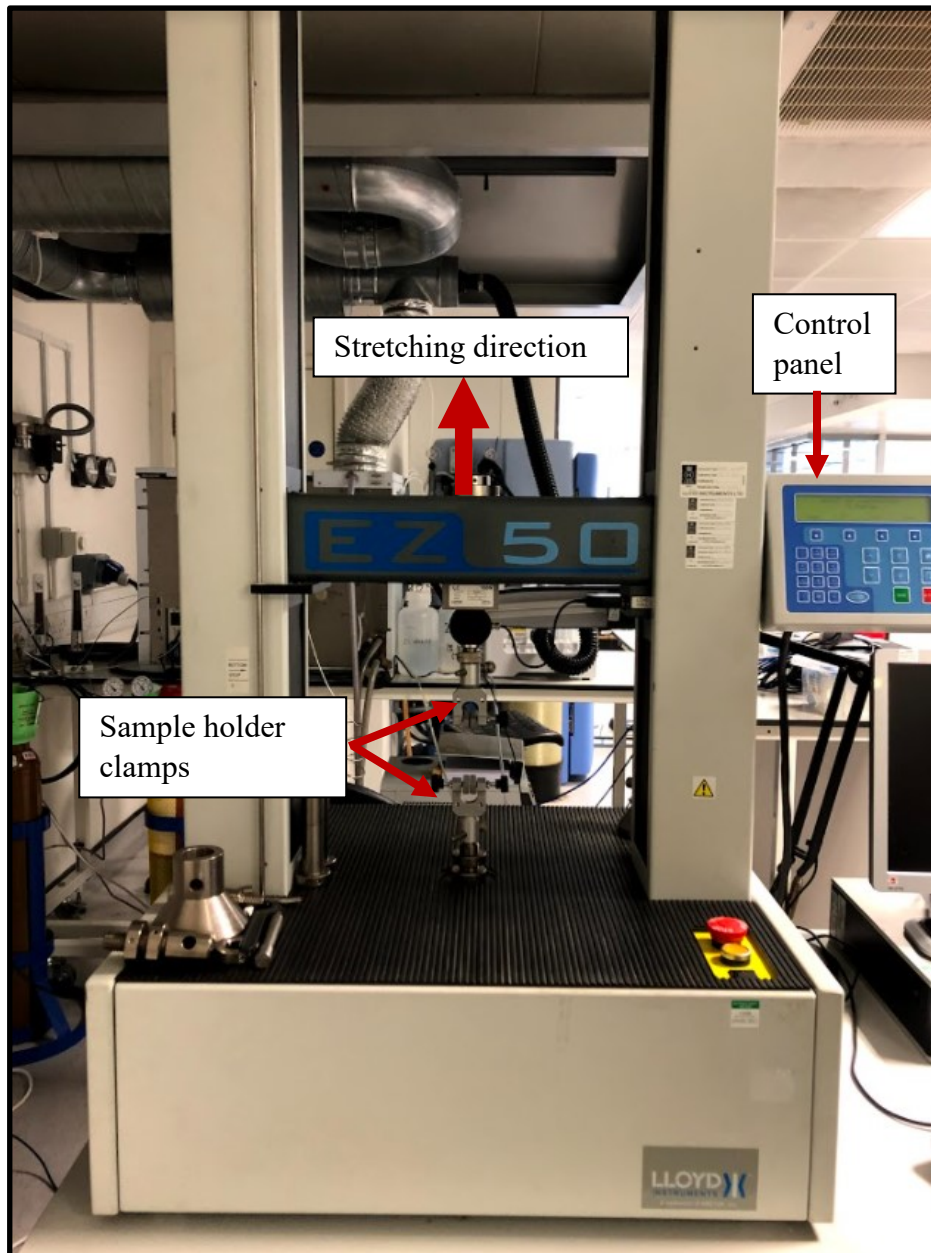


Figure B-4. Lloyd EZ 50 to measure the tensile strength of the membranes

B5- Attenuated Total Reflectance -Fourier Transform Infrared Spectroscopy (ATR-FTIR)

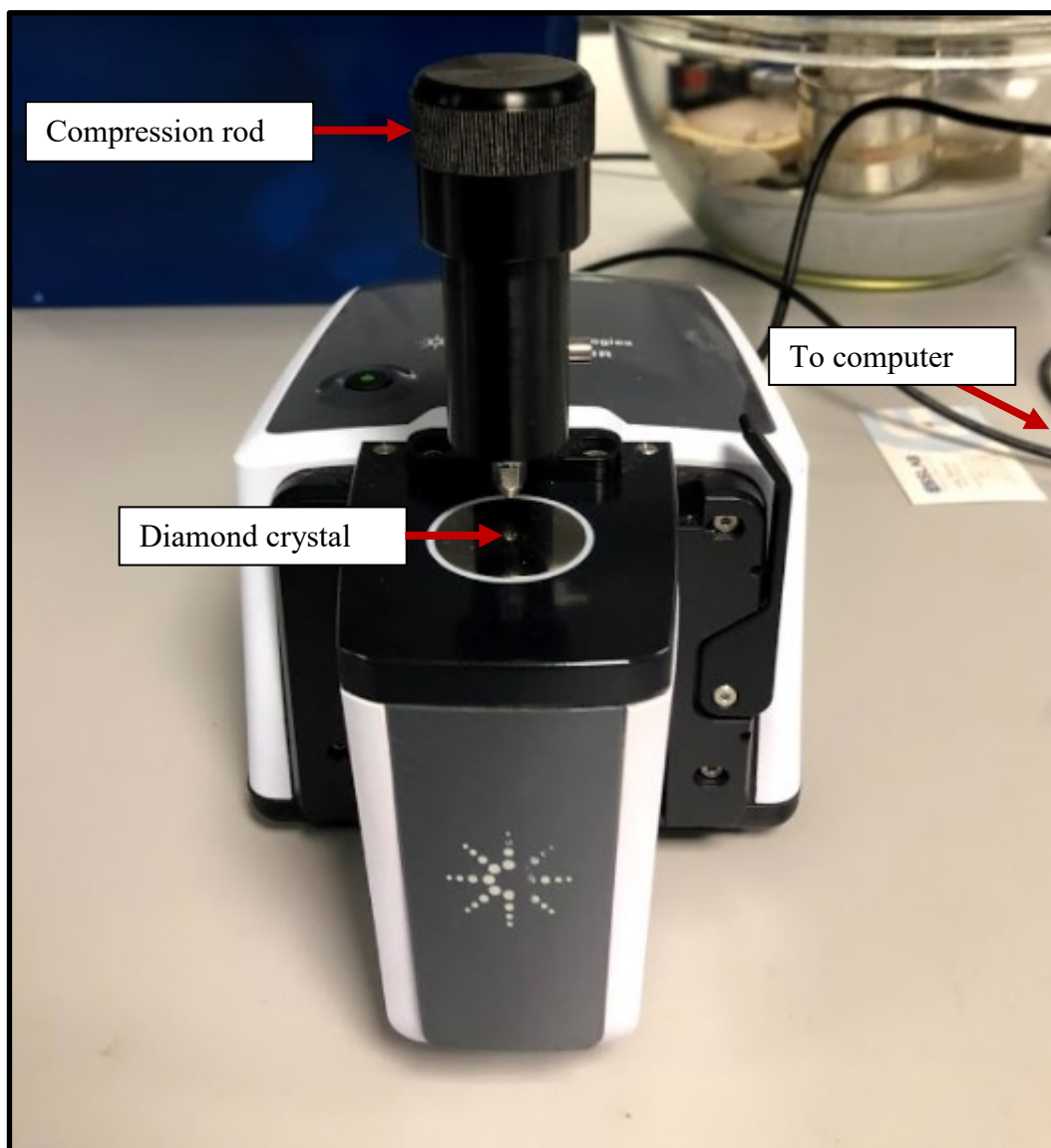


Figure B-5. Agilent Technologies Cary 630 FTIR Spectrometer

B6- Water contact angles

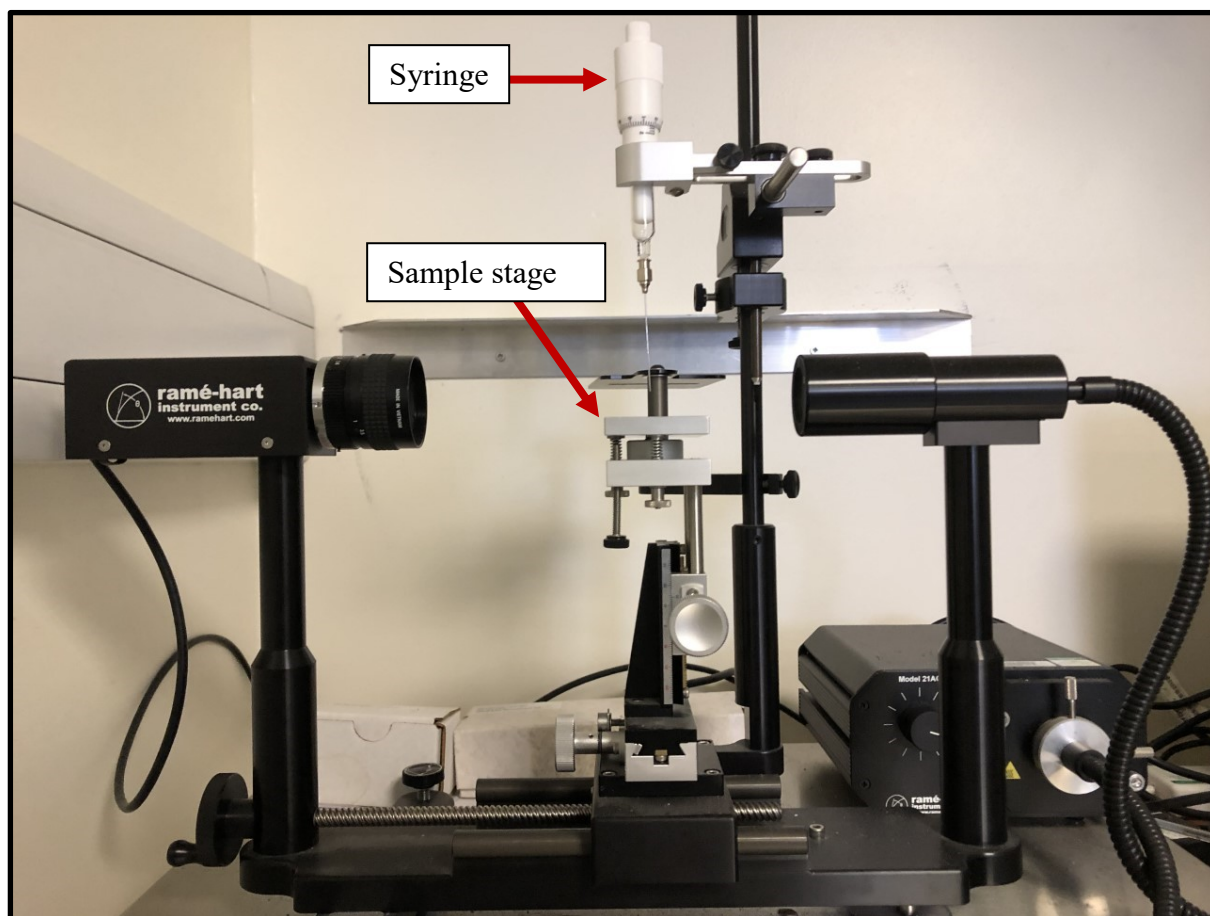


Figure B-6. Ramé-hart Model 590 Advanced Automated Goniometer to measure water contact angles using sessile drop method

B7- Fouling study

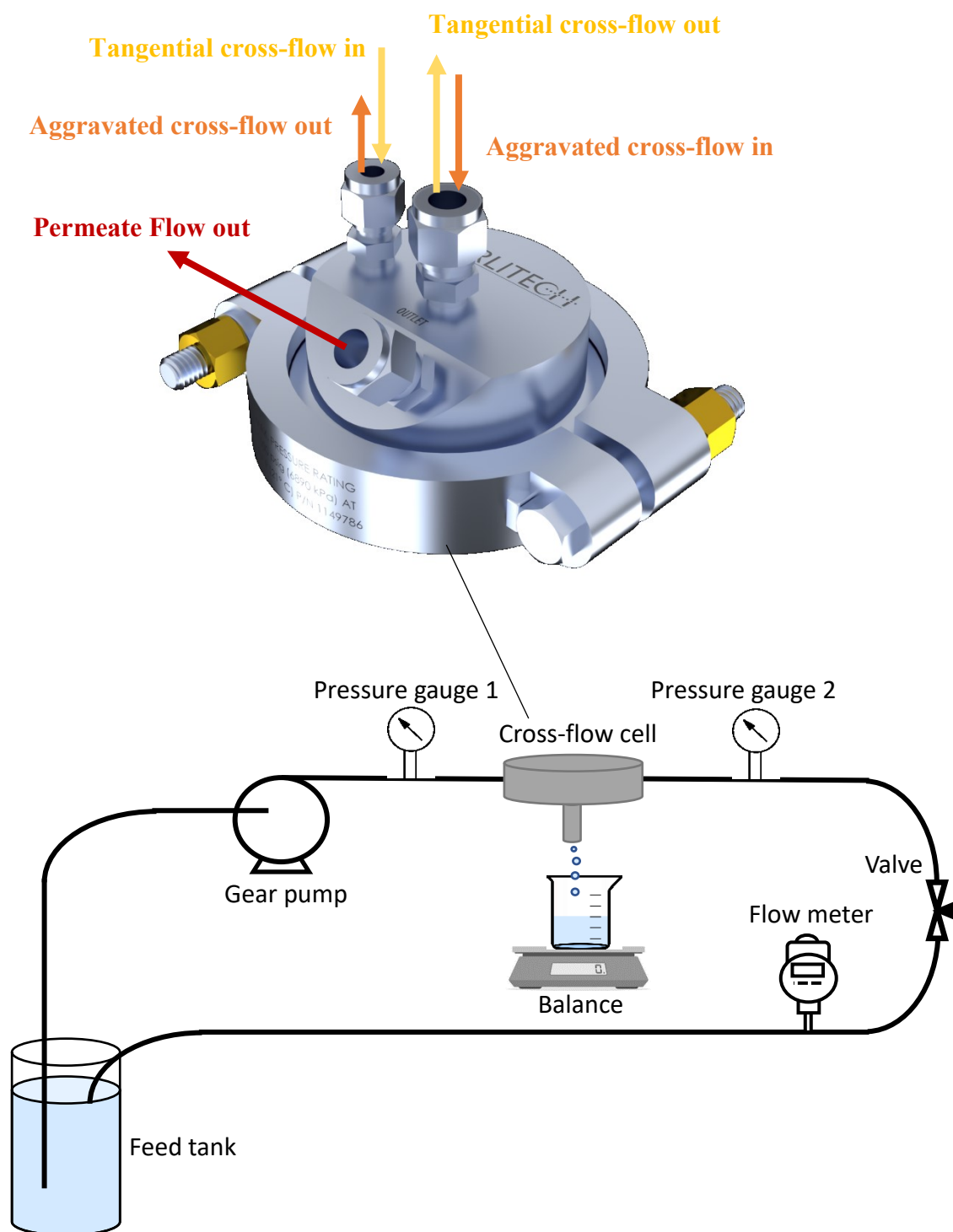


Figure B-7. Cross-flow setup used during the fouling study

B8- BSA Rejection measurement

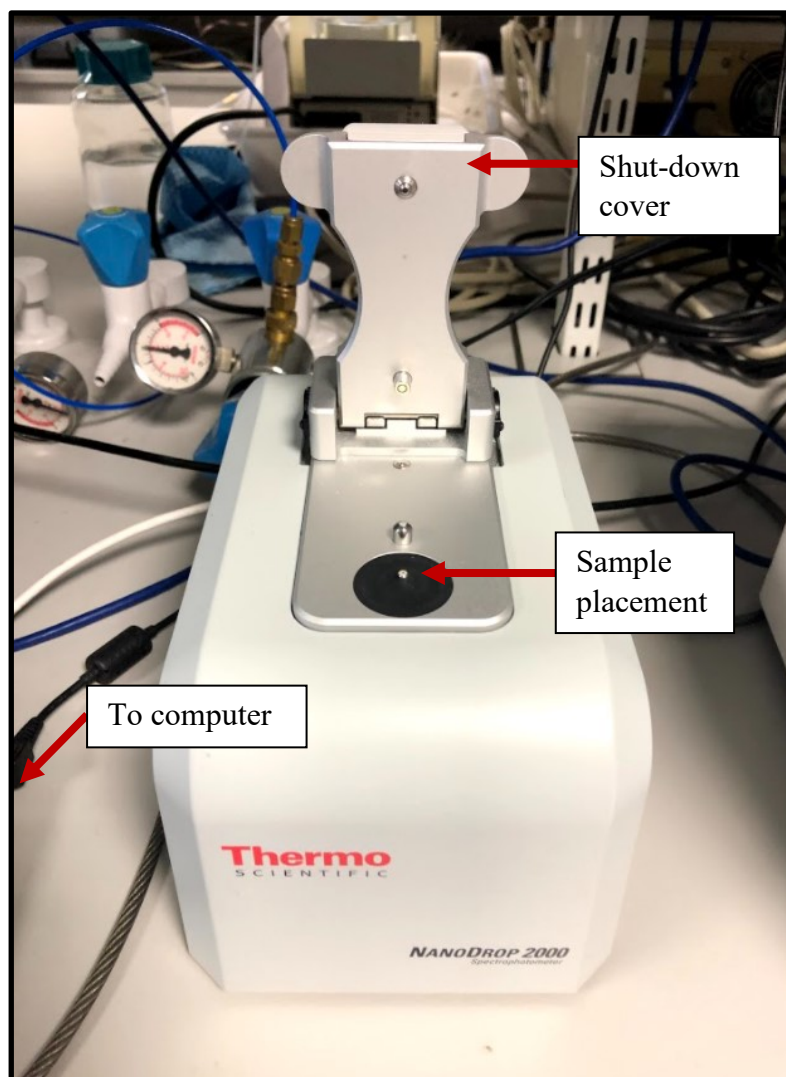


Figure B-8. ThermoFisher Scientific NanoDrop™ 2000 UV-VIS spectrophotometer used to quantify the presence of BSA in the feed and permeate streams

APPENDIX C- Polydopamine (PDA) deposition process

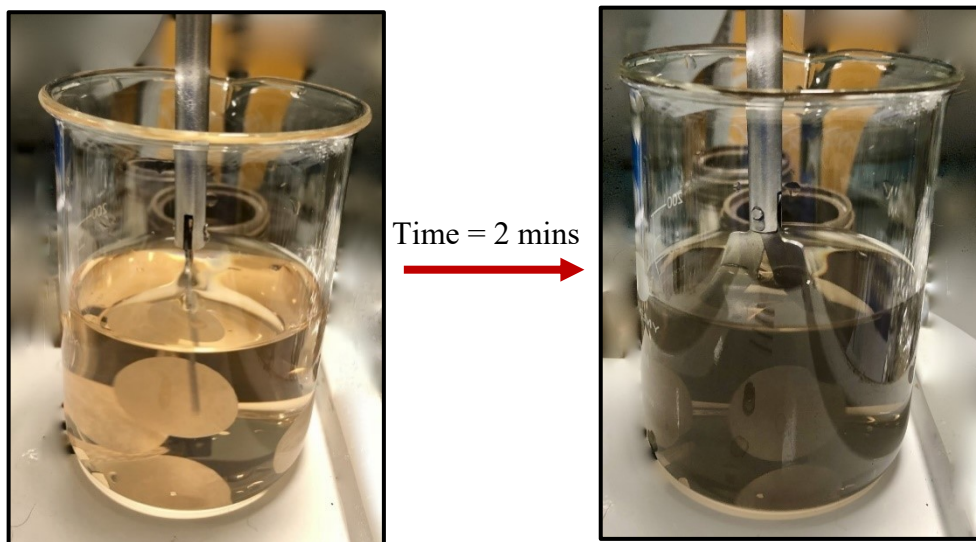


Figure C-1. Change in the colour of the dopamine solution suggesting successful formation of PDA

APPENDIX D- Limitation of Liquid-Liquid Displacement Porometry (LLDP)

LLDP is an effective pore size measurement technique for membranes with pore sizes between 50 to 5nm. In LLDP, the membrane is wetted with a wetting liquid which is subsequently pushed through with a displacing liquid under pressure. As the applied pressure increases, the displacement of the liquid occurs from the larger pores first followed by that from the smaller ones. The flux is measured at each pressure incremental point to finally obtain the breakthrough curve or the wet flow curve. Young-Laplace equation (Equation D-1) is used to calculate the corresponding pore diameter (D) that the liquid penetrates through at a given pressure (P).

$$P = 4\gamma \cos \theta / D \quad \text{Equation D-1}$$

Here γ is the interfacial tension between the two liquids and θ is the contact angle between the wetting liquid and membrane pore. Following the wet flow curve is the dry flow curve where the wetting liquid would have been displaced away by the pushing liquid in all the pores. The dry curve follows a linear relationship between flux and increasing pressure as all pores are now “open”. The schematic representation of the wet flow curve, dry flow curve and $\frac{1}{2}$ dry flow curve is presented in Figure D-1 [1]. The point of intersection between the $\frac{1}{2}$ dry flow curve and the wet flow curve provides the mean flow pore size [1].

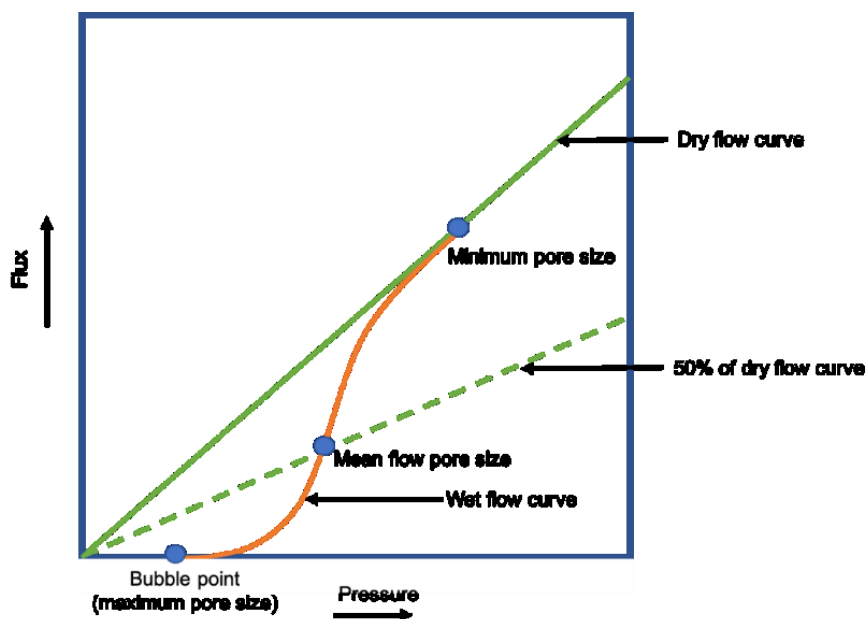


Figure D-1. Variation of flux under applied pressure as measured by the porometer

For pure PVDF samples analysed in our previous studies [2, 3], the mean flow pore sizes were measured using a liquid-liquid displacement porometer (LLP 1500A, Porous Materials Inc., USA). A mixture of 1:1 (v/v) isobutanol-water was prepared which separated into two equilibrated phases - an isobutanol-rich phase and a water-rich phase. The membranes being hydrophobic were pre-wet with the isobutanol-rich phase while the water-rich phase was used to push the wetting liquid out of the pores by the application of pressure. The porometer is then operated as described above. The interfacial tension γ between the two liquids is 1.7 mN/m while the contact angle θ is taken as 0° by assuming complete wetting of the pore by the isobutanol-rich phase.

The mean flow pore size of pure PVDF membrane prepared using 20wt.% polymer dope in DMSO (i.e PVDF_0mins) is measured to be around 30 nm [2, 3]. With the deposition of polydopamine, the interfacial tension of the pore changes, which changes the way the wetting and pushing liquids interact with the surface [4]. The pushing liquid which is composed of a water-rich phase tends to come out a lot sooner at lower pressures, than it otherwise would, as the capillary pressure against the water-rich phase is not as high anymore due to the change in surface hydrophilicity. The contact angle that the wetting liquid makes with the pore channel also changes as illustrated in Figure D-2 and since this cannot be accounted for, it results in an inaccurate over-estimation of the mean flow pore sizes.

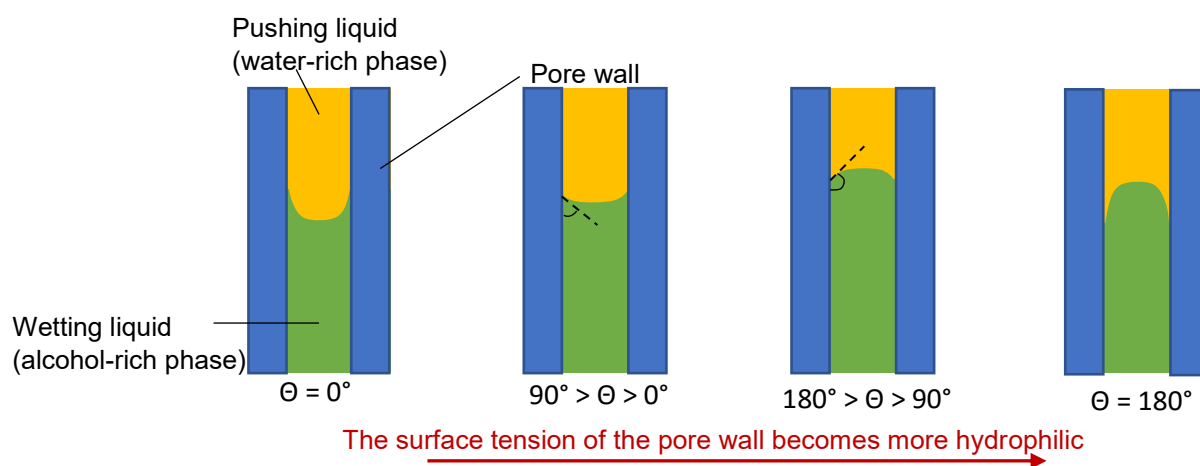


Figure D-2. Change in contact angle between the wetting liquid and the pore wall with an increase in surface hydrophilicity

Gas-liquid porometry could have been a viable alternative, where the pushing fluid is a gas. However, this technique is more suitable for membranes with pore sizes greater than 50 nm [5]. Moreover, this method requires the membranes to be dry before use. Unfortunately, PDA films have been reported to form cracks upon dehydration, which renders this technique

unsuitable for PDA-modified membranes [6]. Another indirect characterisation technique to determine pore sizes is to determine the molecular weight cut off (MWCO) for the membrane. This technique which utilises a range of solutes of different sizes causes pore blocking by the larger sized solutes. This in turn blocks the penetration of many smaller sized solutes, resulting in an underestimated value of the MWCO. From the literature, it was found that a membrane with a pore size of around 14 nm, had an MWCO of 100,000 polyethylene glycol [7]. Since PVDF-CCD membranes have pore sizes around 30 nm, even longer chained compounds would be required and hence this technique was avoided.

The intention was to only know if the pore sizes reduced as a result of PDA deposition, and since the SEM image results quite adequately confirmed this, additional pore size characterisation techniques due to the reasons mentioned above were avoided.

References

1. Friess, K., et al., *1.17 Physical Chemistry Characterization of Polymeric Membranes*, in *Comprehensive Membrane Science and Engineering (Second Edition)*, E. Drioli, L. Giorno, and E. Fontananova, Editors. 2017, Elsevier: Oxford. p. 445-482.
2. Shah, V., B. Wang, and K. Li, *Blending modification to porous polyvinylidene fluoride (PVDF) membranes prepared via combined crystallisation and diffusion (CCD) technique*. Journal of Membrane Science, 2021. **618**: p. 118708.
3. Wang, B., J. Ji, and K. Li, *Crystal nuclei templated nanostructured membranes prepared by solvent crystallization and polymer migration*. Nat Commun, 2016. **7**: p. 12804.
4. Jang, J., Z. Sun, and J.C. Santamarina, *Capillary pressure across a pore throat in the presence of surfactants*. Water Resources Research, 2016. **52**(12): p. 9586-9599.
5. Peinador, R.I., J.I. Calvo, and R. Ben Aim, *Comparison of Capillary Flow Porometry (CFP) and Liquid Extrusion Porometry (LEP) Techniques for the Characterization of Porous and Face Mask Membranes*. Applied Sciences, 2020. **10**(16).
6. Zhang, W.E.I., *Material and Surface Properties of Bio-inspired Polydopamine and its Modified Polypyrrole Functional Nanocomposites*. 2015, UWSpace.
7. Howe, K.J. and M.M. Clark, *Fouling of Microfiltration and Ultrafiltration Membranes by Natural Waters*. Environmental Science & Technology, 2002. **36**(16): p. 3571-3576.

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30	Figure	Figure 2.3	F. Liu, N. A. Hashim, Y. Liu, M. R. M. Abed, and K. Li, "Progress in the production and modification of PVDF membranes," <i>Journal of Membrane Science</i> , vol. 375, no. 1-2, pp. 1-27, 2011, doi: 10.1016/j.memsci.2011.03.014.	© 2011 Elsevier B.V.	16/02/2021	yes	5010931001626
33	Figure	Figure 2.4	F. E. Ahmed, B. S. Lalia, and R. Hashaikeh, "A review on electrospinning for membrane fabrication: Challenges and applications,"	© 2014 Elsevier B.V	16/02/2021	yes	5010940209472

			<i>Desalination</i> , vol. 356, pp. 15-30, 2015, doi: 10.1016/j.desal.2014.09.033.				
37	Figure	Figure 2.5	C. Stropnik, L. Gerič, and B. Žerjal, "Morphology variety and formation mechanisms of polymeric membranes prepared by wet phase inversion," <i>Journal of Applied Polymer Science</i> , vol. 61, no. 10, pp. 1821-1830, 1996/09/06 1996, doi: 10.1002/(SICI)1097-4628(19960906)61:10<1821::AID-APP24>3.0.CO;2-3.	© 1996 John Wiley & Sons, Inc.	16/02/2021	yes	5010940848858
39	Figure	Figure 2.6	A. Bottino, G. Camera-Roda, G. Capannelli, and S. Munari, "The formation of microporous polyvinylidene difluoride membranes by phase separation," <i>Journal of Membrane Science</i> , vol. 57, no. 1, pp. 1-20, 1991/04/01/ 1991, doi: https://doi.org/10.1016/S0376-7388(00)81159-X .	© 1991 Elsevier B.V.	16/02/2021	yes	5010941059301
42	Figure	Figure 2.7	P. Sukitpaneemit and T. S. Chung, "Molecular elucidation of morphology and mechanical properties of PVDF hollow fiber membranes	© 2009 Elsevier B.V.	16/02/2021	yes	5010941367914

			from aspects of phase inversion, crystallization and rheology," <i>Journal of Membrane Science</i> , Article vol. 340, no. 1-2, pp. 192-205, 2009, doi: 10.1016/j.memsci.2009.05.029.				
43	Figure	Figure 2.8	E. Drioli, L. Giorno, and E. Fontananova, <i>Comprehensive Membrane Science and Engineering</i> . Elsevier Science, 2017.	© 2015 American Institute of Chemical Engineers	16/02/2021	yes	5011240951607
54	Table	Table 2.1	G.-d. Kang and Y.-m. Cao, "Application and modification of poly(vinylidene fluoride) (PVDF) membranes – A review," <i>Journal of Membrane Science</i> , vol. 463, pp. 145-165, 2014/08/01/ 2014, doi: https://doi.org/10.1016/j.memsci.2014.03.055 .	Copyright © 2014 Elsevier B.V.	16/02/2021	yes	5011260233060