



Review

Progress in the production and modification of PVDF membranes

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ABSTRACT

This article provides a comprehensive overview of recent progress on the production and modification of poly(vinylidene fluoride) (PVDF) membranes for liquid–liquid or liquid–solid separation. The crystalline properties, thermal stability and chemical resistance were firstly considered in this review, followed by the production methods of PVDF membranes via phase inversion including immersion precipitation and thermally induced phase separation. Various hydrophilic modification approaches such as surface modification and blending modification for improving the fouling resistance of PVDF membranes were subsequently reviewed. Finally, in the light of the anticipated role of PVDF as a superior membrane material, future prospects on the production and modification of PVDF membranes were suggested.

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1. Introduction

Since 1960s, when the first commercial membrane was invented via phase inversion method [1], significant milestones in the development of membrane separation technologies have been scientifically and commercially achieved. Following the remarkable invention, several major processes including reverse osmosis, ultrafiltration, microfiltration and gas separation have been established in large-scale membrane production. Nowadays, the applications of membrane technologies cover almost every industrial sector including environmental, electronic, energy, chemical and biotechnologies areas.

Currently, much effort is being devoted to improve the performance of the existing membranes in terms of anti-fouling properties, high mechanical strength and good chemical resistance. The emergence of new membrane processes such as membrane contactor, membrane distillation or membrane reactor has also received great attention from researchers in the recent years. These developments have been motivated by the needs in the industrial sectors to reduce the overall operational costs compared to the conventional separation processes as well as broaden the membrane applications.

Poly(vinylidene fluoride) (PVDF) has received great attention as a membrane material with regard to its outstanding properties such as high mechanical strength, thermal stability, chemical resistance, and high hydrophobicity, compared to other commercialised polymeric materials. PVDF membranes have been extensively applied in ultrafiltration and microfiltration for general separation purposes, and are currently being explored as potential candidates in the applications of membrane contactor and membrane distillation [2–10].

Several studies have reported the developments and applications of PVDF membranes since the 1980s [11–14]. To date, remarkable progress has been made in the fabrications of PVDF membranes with high performance for the applications in membrane distillation, membrane contactor as well as in wastewater treatment. Nevertheless, fabrication of high performance PVDF membrane remains challenging and is hard to be achieved. This leads to the present article which aims to comprehensively review available literature associated with the progress and production of PVDF membranes particularly in flat sheet and hollow fibre configurations. Special emphasis is given on the effects of various parameters involved in the preparation of membranes from phase inversion process to hydrophilic modification of PVDF membranes.

2. Considerations of using PVDF as a membrane material

In the recent years, PVDF has become one of the more popular membrane materials. Comparing with other materials such as polysulfone (PS), polyethersulfone (PES) and polyimide (PI), PVDF is relatively more hydrophobic, although the hydrophobicity may not be as high as polypropylene (PP) and polytetrafluoroethylene (PTFE). The hydrophobicity of materials is often associated with their surface tensions; the critical surface tensions of major polymeric membrane materials are listed in Table 1 [13]. Since the fabrication of PP and PTFE membranes via phase inversion process is limited due to the complexity in solvent selection, PVDF remains the best option of membrane material for the applications such as membrane distillation and membrane contactor [9].

This is because PVDF easily dissolves in common organic solvents; as a result, porous PVDF membranes can be produced via phase inversion method by a simple immersion precipitation process. Furthermore, the excellent thermal stability of PVDF has made it interesting as a membrane material in a wide range of industrial applications.

Table 1

Critical surface tensions of major polymeric membrane materials [13].

Polymer	Critical surface tension (dynes/cm)
Polyacrylonitrile (PAN)	44
Polysulfone (PS)	41
Polyphenylene oxide (PPO)	41
Polyethylene (PE)	31
Polypropylene (PP)	29
Polyvinylidene fluoride (PVDF)	25–28.5
Polyfluoroethylene (PFE)	22
Polytetrafluoroethylene (PTFE)	18.5
Fluorinated ethylene propylene (FEP)	16
Ethyltetrafluoroethylene (ETFE)	17

PVDF is also advantageous over other membrane materials due to its high mechanical strength and excellent chemical resistance, in which these properties make it suitable for wastewater treatment. By possessing low level of extractables, PVDF can be considered as a pure polymer; which makes it a suitable candidate in biomedical and bio-separation applications. Unlike other crystalline polymers, PVDF exhibits thermodynamic compatibility with other polymers such as poly(methyl methacrylate) (PMMA) over a wide range of blend compositions [15,16], where this characteristic can be useful in the fabrication of membrane with the desired properties. PVDF can be further chemically modified to obtain some specific functions [17,18], and can be cross-linked when subjected to electron beam radiation or gamma radiation [19,20].

Beside PVDF, there are some other fluorocopolymers which can be used as membrane materials, such as poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)), poly(vinylidene difluoride-co-chlorotrifluoroethylene) (P(VDF-CTFE)), etc. P(VDF-HFP) seems to be the more promising membrane material than PVDF for the application of membrane contactor, because the addition of an amorphous phase of hexafluoropropylene (HFP) group into the main constituent VDF blocks increases the fluorine content, making P(VDF-HFP) more hydrophobic than PVDF material [21–24]. P(VDF-HFP) can also be applied in the field of rechargeable lithium-ion battery as a separator material because P(VDF-HFP) contains more amorphous domains capable of trapping a large amount of liquid electrolytes [25]. P(VDF-CTFE) membranes are modified by grafting of poly(styrene sulfonic acid) or poly(ethylene glycol) methyl ether methacrylate (PEGMA), which can be used for ultrafiltration membranes or proton conducting membranes [26,27].

2.1. Crystalline properties of PVDF

PVDF is a semicrystalline polymer that usually contains 59.4 wt% fluorine and 3 wt% hydrogen [28]. The commercial PVDF is generally produced by polymerisation in emulsion or suspension using free radical initiators, forming a repeating unit of $-\text{CH}_2-\text{CF}_2-$. The spatial arrangement of the CH_2 and CF_2 groups along the polymer chains can contribute to the unique properties of PVDF generated from its crystalline structure.

Generally, polymer crystallinity and the resultant membrane morphology are among important factors in determining the mechanical strength properties, as well as the impact resistance of the membranes. PVDF chains can crystallise into at least four distinct phases or forms, which are α (form II), β (form I), γ (form III) and δ (form IV) [29,30]. It is well known that the most common polymorph of PVDF is α -phase with the molecular chain conformation of trans-gauche (TGTG') placing the H and F atoms alternately on each side of the chain. The degree of the crystallinity of PVDF can range between 35% and 70%, and can be determined by measuring the specific volume of crystalline and amorphous phases

[31,32]. Crystallisation of PVDF is controlled by a number of variables including molecular weight, molecular weight distribution, polymerisation method, thermal history and cooling rates [33]. It is important to understand the effects of fabrication conditions on the crystalline phase formed in order to have a proper control on the properties of the resultant membrane.

Cheng investigated the effect of precipitation temperature on the morphology and crystalline structure of PVDF membranes prepared by 1-octanol/DMF/PVDF and water/DMF/PVDF systems [34]. Different temperatures of 25 °C and 65 °C were employed in the coagulation bath during membrane formation. Because crystallisation had preceded the liquid–liquid demixing, a symmetric membrane with uniform spherical PVDF crystallites was obtained at lower temperature. On the other hand, an asymmetric membrane comprised of dense skin layer and cellular structure was formed at a higher temperature as a result of liquid–liquid demixing. The crystallites present in the resultant membrane are believed to be a mixture of α and β forms (which is largely in β -form).

In addition, Wang et al. observed a similar effect of coagulation bath temperature on the crystallinity, where the membrane fabricated from 15 °C bath temperature exhibited greater crystallinity than the one prepared from 60 °C coagulation bath [35]. They also found that membrane precipitated at 60 °C only showed a typical α crystal structure, while at 15 °C the PVDF crystallites consisted of a mixture of α and β crystal forms. Other than the precipitation temperature, coagulation medium is another factor affecting the crystal structure and morphology of PVDF membrane. Cheng et al. discovered that the presence of 1-octanol in both the coagulation bath and casting solution resulted in the formation of PVDF membrane dominated by the crystallisation process [36]. When the crystallisation precedes liquid–liquid demixing, the size of particulate formed was observed to have decreased with increasing 1-octanol content in dope solution.

There have been studies reporting the effect of polymer dissolving temperatures during the preparation of membrane solution on the morphology and structure of PVDF membrane [37,38]. Lin et al. dissolved PVDF in N,N-dimethylformamide (DMF) at different temperatures and immersed the cast membranes in 1-octanol coagulation bath. Interestingly, they observed the formation of larger spherulites in membrane morphology when the dissolving temperature was increased, though the crystallinity of all membranes remained unaffected and all membranes exhibited α -type crystal structure [37]. Wang et al. also observed remarkable changes on the morphology of PVDF membranes prepared from various temperatures in N,N-dimethylacetamide (DMAc) with water as a coagulation medium [38]. In their study, the cross sections of all membranes were found to be composed of an interconnected structure with cavities and are of α -type crystal structure, though the size of the cavities becomes larger with the increase in the dissolving temperatures.

Several methods have been identified in measuring the degree of different crystal forms in PVDF. Benz and Euler determined the crystalline phase compositions by quantitatively measuring the degree of α , β , and γ crystallinity in PVDF thin films using infrared (IR) spectroscopy [39]. Gregorio applied Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) to determine the three crystalline phases formed in films, prepared at different conditions [40]. Similar methods have been employed by Buonomenna et al. to identify the crystalline phases of the membranes prepared from various alcohols as the coagulants [41]. Detailed investigations on the formation of crystalline structure at different membrane formation conditions have been made, and the relationship between crystallisation and membrane properties such as morphology and mechanical strength has been discussed in their studies.

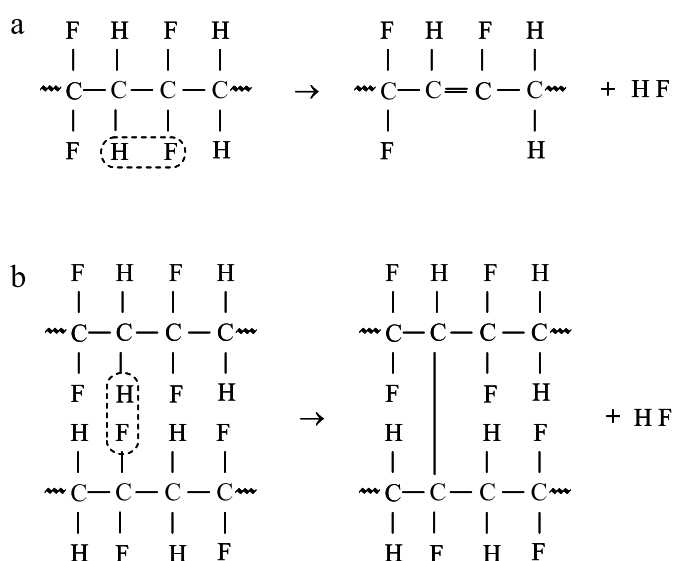


Fig. 1. Schematic diagram of the mechanism of dehydrofluorination in PVDF (a) formation of double bonds in the chain and (b) crosslinking of the polymer [42].

2.2. Thermal stability of PVDF

It is well known that the excellent thermal stability of PVDF has made it popular in a wide range of applications. In general, fluoropolymers are thermally more stable than hydrocarbon polymers. The high electronegativity of fluorine atoms on the chain and the high bond dissociation energy of the C–F bond provide the high stability of the fluoropolymers. Although generally stable and inert, PVDF has been observed to experience degradation during high temperature operations. Madorsky and co-workers were first to extensively study the thermal degradation of PVDF at moderate and high temperatures in vacuum [42]. Their results from the pyrolysis under vacuum demonstrate that the mechanism of thermal degradation in PVDF predominated by the loss of hydrogen fluoride (HF), or occasionally referred as dehydrofluorination, consequently led to several chemical reactions including the formation of carbon–carbon double bonds (–C=C–) or cross-linking of the polymer. Fig. 1 shows the schematic diagram of the possible mechanisms of dehydrofluorination in PVDF. Other possible reactions such as the formation of free radicals were also proposed by Madorsky.

Nguyen provided a systematic review on the thermal stabilities of PVDF based on the available literatures that reported about their investigations on the degradation processes conducted at early stages [43]. General agreement was made based on the literatures concerning the mechanism of the PVDF polymer degradation process. PVDF is thermally degraded primarily by the evolution of HF (dehydrofluorination) and followed by the formation of double bonds.

Meanwhile, Lovinger and Reed observed an inhomogeneous thermal degradation of PVDF, which had been crystallised at a high temperature (~160 °C) [44]. They discovered that various spherulitic forms in PVDF degraded differently, causing an inhomogeneous discolouration of the samples. This degradation process took place predominantly in the crystalline regions and not in the amorphous segment, which is an uncommon phenomenon observed in case of other polymers. The primary mechanism of the degradation process was dominated by the elimination of HF with a little chain scission or cross-linking. The compositional and conformational changes on the molecular chains resulted from the heat treatment were demonstrated by the presence of numerous

extra absorption bands in the infrared spectrum as a result of the crystallising process for a prolonged period of time.

While the thermal degradation of polymers has been widely investigated using various methods such as thermogravimetric analysis and pyrolysis gas chromatography, Furusho and co-workers conducted a study on the thermal degradation of several halogen-containing polymers including PVDF, using a Torsional Braid Analysis (TBA) method [45]. PVDF was observed to be among the most thermally stable halogen-containing polymers in their study. Benzinger et al. evaluated the thermal stability of a commercial Kynar PVDF ultrafiltration membrane using spiral-wound modules at a higher temperature [46]. During continuous operation at 85.6 °C, while keeping the pressure constant for 7 months, no evidence of thermal degradation was observed on the PVDF membrane.

Table 2 shows the thermal properties of the PVDF material mainly used in the membrane fabrications. A comparison of the PVDF thermal stability with its competitive materials including polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), polysulfone (PS), polyethersulfone (PES) and polyimide (PI) are also provided in the table.

2.3. Chemical resistance of PVDF

PVDF generally possesses distinction chemical stability against most of the chemicals, including a wide range of harsh chemicals such as halogens and oxidants, inorganic acids, as well as aliphatic, aromatic and chlorinated solvents. Based on the information provided by one of the major PVDF suppliers, Arkema Inc. (Kynar® PVDF Chemical Resistance, www.arkema-inc.com), the chemical stability of PVDF against the above mentioned chemicals can be considered as excellent. However, the excellent chemical stability of PVDF does not particularly apply to strong base solutions or to esters and ketones. Therefore, with regard to the application of PVDF membranes, especially in membrane contactors for acid gas absorption or wastewater treatment, where PVDF membranes are being exposed to strong alkaline solution and subjected to frequent chemical cleaning involving a significant amount of alkaline, the stability of PVDF membranes is of a particular concern.

To date, only a few studies have been found with respect to the chemical stabilities of PVDF membranes, to be associated with such applications. Nguyen provided a comprehensive review on the degradation of PVDF, yet little information about the degradation of PVDF caused by alkaline solutions was mentioned [43]. Early investigations reported the observations of the discolouration of PVDF from white to brown and finally black upon immersion into alkaline solutions for a few hours [47,48]. Shinohara observed that the colour of oxyfluorinated PVDF film became darker as a result of the hot alkali treatment, demonstrating the formation of C=C bonds caused by the dehydrofluorination in polymer chain [48]. Komaki and Otsu observed that PVDF film shrinks and becomes brittle with a deep colour when immersed into sodium hydroxide solution containing ethanol [49]. Further investigations by Hoa and Ouellette demonstrated that the chemical attack of sodium hydroxide on PVDF could be accelerated by imposing strain, and cracks could occur when sufficient strain is applied [50]. They indicated that NaOH solution chemically attacked PVDF in α conformation and observed discolouration of PVDF specimens upon immersion in NaOH solution.

Meanwhile, Kise and Ogata studied the reaction between PVDF powder and aqueous NaOH solutions with or without the presence of quaternary ammonium or phosphonium halides as phase transfer catalysts [51]. The colour change of PVDF was observed after a few hours of immersion in an aqueous NaOH solution at a high temperature, and the reaction had been accelerated with the presence of tetrabutylammonium bromide (TBAB) as a catalyst yielding a fine

Table 2
Thermal stabilities of PVDF compared with various polymers.

Thermal stability	PVDF	PP	PE	PTFE	PS	PES	PI	P(VDF-HFP)	P(VDF-CTFE)
Melting point (°C)	140–170	130–170	118–146	310–385		340–390	350–390	141–145	
Glass transition temperature (°C)	–41/–38	2.0/10	–118/–127		185	225	120/370	–42/–39	–28
Thermal stability, 1% mass loss, in air (°C)	375					400		375	320–340
Linear thermal expansion coefficient 10 ^{–6} /°C	50–103 or 120–140	140–180		14–250	28.8–103	55	55		

black powder. Fourier transform infra-red (FTIR) results demonstrated the formation of carbon–carbon double and triple bonds due to the elimination of HF molecules. Similar conclusions were drawn by Wegener et al. in their study on PVDF film dissolved in NaOH as a catalyst in dimethylsulfoxide (DMSO) and acetone mixture [52]. The dehydrofluorination of PVDF led to partial degradation of the fluorocarbons and to the formation of carbon–carbon double and triple bonds, as examined by UV–vis spectroscopy and FTIR analyses.

Kuhn et al. employed FTIR-ATR (Attenuated Total Reflectance) technique in examining the structure of dehydrofluorinated PVDF film surface by aqueous NaOH solution with the use of tetrabutylammonium hydrogen sulfate (TBAH) as phase transfer catalysts [53]. Their results revealed that the elimination of the HF unit resulted in the formation of carbon–carbon double bonds with some formations of conjugated double bonds, though the conjugation might be incomplete due to the presence of head-to-head and tail-to-tail chain irregularities.

A long term study on the effect of different types of acids, bases, and oxidants including NaOH solution on PVDF membrane was conducted by Benzinger et al. [46]. It was found that PVDF membranes have an excellent stability to harsh chemicals such as acids, strong oxidants and many organic solvents, but poor stability when exposed to a concentrated NaOH solution for three months. Similar findings were obtained by Vigo et al. on the effect of NaOH solutions on PVDF membranes [54]. While no particular effect was observed on the performance of PVDF membranes which had been exposed to water, wool scouring wastewater, acids, calcium chloride and sodium bisulfite at different concentrations, the performance of PVDF membranes was affected by the concentrated sodium hydroxide and sodium hypochlorite solutions. In addition, the mechanical strength of the membranes tested by bursting pressure was also reduced when exposed to concentrated sodium hydroxide and sodium hypochlorite.

A systematic study on the chemical stability of PVDF hollow fibre membranes made of different types of commercial PVDF raw materials in NaOH solution has been conducted by Li and co-workers [55]. In their study, hollow fibres were spun from several commercial PVDF raw materials, namely Kynar 761, Solef 1015 and Solef 6010 and treated with different concentrations of NaOH aqueous solution at 20 °C and 70 °C. It has been demonstrated that PVDF membranes prepared from different types of raw materials exhibit different levels of degradation due the attack by NaOH, depending on the membrane surface area.

Based on the information described as above, several conclusions can be made: (1) sodium hydroxide solution chemically attacks PVDF in α conformation and decolourised it; (2) the chemical attack/reaction of sodium hydroxide on PVDF could be further accelerated by the increase in temperature and the presence of catalysts. There are many factors that can affect the chemical resistance of PVDF membranes, including the exposure time, chemical concentrations, temperature, pressure, frequency of the attack cycles, and the type of mechanical stress imposed. Related research will be of significance but remains challenging.

2.4. Comparison of currently available materials

Arkema Inc. (or previously known as Atofina Chemicals Inc. or Elf Atochem) and Solvay are the two major worldwide suppliers of PVDF, especially for membrane fabrications. There are also several other localised PVDF manufacturers in other countries, including Japan and China. Table 3 provides the detailed information about the PVDF materials mainly employed in membrane fabrications.

Table 3
Properties of PVDF materials from two major suppliers for membrane fabrication.

Supplier	Kynar 760/761	Kynar 740	Kynar 461/301F	Kynar HSV900	Kynar flex 2801	Solef 1015	Solef 6010	Hylar 460/461
Type of polymer	Atofina Chemicals Inc. Homopolymer	Elf Atochem Homopolymer	Arkema Inc. Homopolymer	Arkema Inc. Homopolymer	Arkema Inc. Copolymer	Solvay Homopolymer	Solvay Homopolymer	Solvay Homopolymer
Physical properties								
M_n/M_w *	440,000	254,000	–	–	–	573,000	322,000	540,000
Density (g/ml)	1.77–1.79	1.77–1.79	1.75–1.77	1.77–1.79	1.76–1.79	–	1.78	1.76
Intrinsic viscosity (dL/g)	–	0.881	–	–	–	–	–	–
Melt viscosity (kPa·s)@100 s ^{−1} and 232 °C	23–29	15–23	23–30	32–54	23–27	–	–	–
Water absorption	0.01–0.03	0.01–0.03	0.02–0.04	0.01–0.03	0.03–0.05	<0.04	<0.04	0.02
Mechanical test@23 °C, 50 mm/min								
Tensile stress at yield (MPa)	45–55	45–55	34–52	45–55	20–34	53–57	53–57	48
Tensile stress at break (MPa)	34–55	34–55	31–48	34–55	17–34	35–50	35–50	41
Elongation at yield (%)	5–10	5–10	10–15	5–10	10–20	5–10	5–10	10
Elongation at break (%)	50–200	50–200	50–250	50–200	200–400	20–50	20–50	100
Tensile modulus (MPa)	1379–2310	1379–2310	1034–1379	1379–2310	551–896	2200	2400	1310
Thermal stability								
Melting point (°C)	165–172	165–172	155–160	162–172	140–145	173	173	160
Crystallising point (°C)	–40/–38	–40/–38	–40/–38	–40/–38	–41/–39	140	138	132
Glass transition temperature, T_g (°C)	375	375	375	375	375	–30	–32	–39
Thermal stability, 1 wt% mass loss/in air (°C)	66–80	66–80	50–70	66–80	70–103	375–400	400	375
Linear thermal expansion coefficient 10 ^{−6} /°C	–	–	–	–	–	120–140	120–140	126

Table 4

Hansen solubility parameters and boiling point of common solvents for PVDF [66,69].

Solvents	Dispersion parameter $\delta_{d,P}$ (MPa ^{1/2})	Polar parameter $\delta_{p,P}$ (MPa ^{1/2})	Hydrogen bonding parameter $\delta_{h,P}$ (MPa ^{1/2})	Total solubility parameter $\delta_{t,P}$ (MPa ^{1/2})	Boiling point (°C)
N,N-Dimethylacetamide (DMAc)	16.8	11.5	10.2	22.7	165.0
N,N-Dimethylformamide (DMF)	17.4	13.7	11.3	24.8	153.0
Dimethylsulfoxide (DMSO)	18.4	16.4	10.2	26.7	189.0
Hexamethyl phosphoramide (HMPA)	18.4	8.6	11.3	23.2	232.5
N-Methyl-2-pyrrolidone (NMP)	18.0	12.3	7.2	22.9	202.0
Tetramethylurea (TMU)	16.8	8.2	11.1	21.7	176.5
Triethyl phosphate (TEP)	16.8	11.5	9.2	22.3	215.5
Trimethyl phosphate (TMP)	16.8	16.0	10.2	22.3	197.2
Acetone (Ac)					56.1
Tetrahydrofuran (THF)					65.0

3. Preparation of PVDF membranes

The preparation of PVDF membranes had started mainly from the early 1980s [11,12,14]. Several methods are employed in the fabrication of PVDF membranes and these include phase inversion, use of inorganic particles as a filler or as an additive, sintering, and track etching [12,14,56–61]. To date, most of the commercial membranes are produced via phase inversion methods mainly because of its simplicity and flexible production scales. Thus, this helps to maintain the low cost of production [62,63]. This method can also be considered as the main method for the preparation of PVDF membranes and has attracted great attention among researchers [12,64–67]. This section provides a review on the preparation of PVDF membranes via phase inversion method, and a brief discussion on other fabrication methods as mentioned above.

3.1. Phase inversion

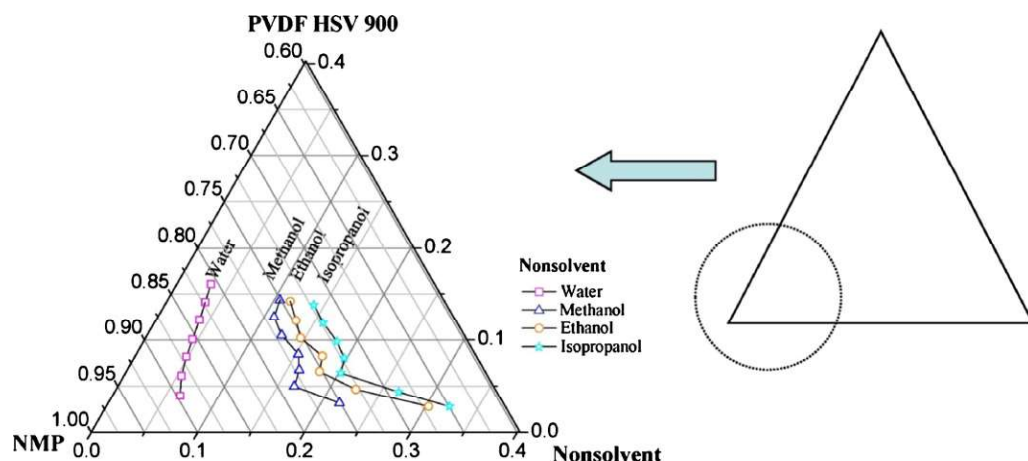
Phase inversion can be described as a demixing process whereby the initially homogeneous polymer solution is transformed in a controlled manner from a liquid to a solid state [63]. This transformation can be accomplished in several ways, namely (a) thermally induced phase separation (TIPS); (b) controlled evaporation of solvent from three component systems; (c) precipitation from the vapour phase and (d) immersion precipitation (IP).

However, among these techniques, TIPS and IP are the two most commonly employed methods in the fabrication of polymeric membranes such as PVDF. One of the main difficulties that limits the successful casting of phase inversion membranes is the lack of a predictable and systematic method in selecting solvent systems [68].

Solvent plays a very important role in determining the ultimate membrane properties and performance. With proper selection of solvent, the high polymer chain mobility could be maintained, which is directly influenced by both polymer–solvent and polymer–polymer interactions. When polymer molecules dissolve easily in a good solvent, a uniformly distributed polymer configuration could be formed. On the other hand, poor solvent results in the aggregation of polymer molecules. Table 4 lists the identified good solvents of PVDF mainly used in the immersion precipitation method and their boiling points [69]. In this section, major emphasis is placed on the preparation of PVDF membranes via IP and TIPS process.

3.1.1. Immersion precipitation

Immersion precipitation (IP) is a process where a polymer solution is cast on a suitable support, then immersed in a coagulation bath containing a non-solvent. The exchange of the solvent in polymer solution with the non-solvent from the coagulation bath results in the phase separation. IP can be considered as the main technique in the fabrication of industrial asymmetric membranes due to the simplicity of its process. Most of the available PVDF membranes are also produced via IP method because of its ease of dissolution in common organic solvents. As a semi-crystalline polymer, the phase separation behaviour of a PVDF polymer is more complicated than an amorphous polymer such as polysulfone and polyethersulfone [70]. Research and development of PVDF membranes prepared via immersion precipitation process have been actively pursued by a number of researchers, focusing on the effect of various preparation conditions on membrane morphology and performance, as well as the relationship between membrane structure with its formation process [12,65,66,71,72].

**Fig. 2.** Phase diagram of ternary PVDF/NMP/non-solvent systems at 25 °C [73].

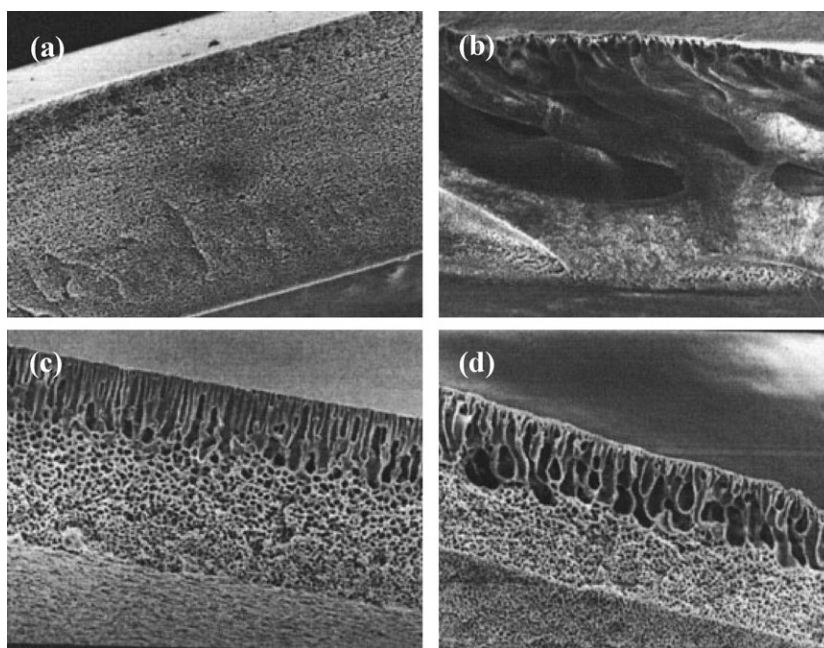


Fig. 3. Cross section images of PVDF membranes formed by the following solvents: (a) TEP; (b) NMP; (c) DMF and (d) DMAc [75].

Sukitpaneenit and Chung investigated the thermodynamics of the phase inversion process of PVDF membrane through phase diagrams [73]. Fig. 2 shows the ternary phase diagrams of PVDF/NMP/non-solvent systems at 25 °C, which are constructed based on the cloud-point measurements. The gelation boundary for the PVDF/NMP/water system is closer to the polymer–solvent axis as compared to the other PVDF/NMP/non-solvent systems. In other words, only a small amount of water is needed to disturb the solution system equilibrium and induce the polymer precipitation. The results suggest that the thermodynamic stability of the PVDF/NMP/non-solvent systems follows the sequence: water < methanol < ethanol < IPA. Therefore, water is a strong non-solvent while alcohols are weak non-solvents for the PVDF/NMP system.

The effect of various parameters on the morphology and performance of PVDF flat sheet and hollow fibre membranes are described herein.

3.1.1.1. Effect of solvents on membrane morphology. As mentioned in the previous section (Section 3.1), solvent plays an important role in determining the ultimate membrane morphology and performance. Munari et al. and Bottino et al. performed excellent fundamental work on the essential information of PVDF polymer–solvent interactions [12,66,74]. Based on Hansen solubility parameter, Bottino et al. identified eight organic solvents out of forty-six that had been screened to be good solvents for PVDF polymer (based on the testing conducted with PVDF Forafon 1000 HD) [74]. These include N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), hexamethylphosphoramide (HMPA), tetramethylurea (TMU), triethylphosphate (TEP), and trimethylphosphate (TMP). Among these solvents, DMAc, NMP, DMF and DMSO have been extensively employed as high boiling point strong solvents, while acetone or tetrahydrofuran (THF) has been used as the low boiling point weak solvent in casting PVDF membranes [11,12,66,74].

Based on Bottino's investigation, the solubility parameters of the identified good solvents for PVDF are tabulated in Table 4 [66]. By employing eight different types of solvents, various structures

of PVDF flat sheet membranes were obtained. Their experimental results demonstrated that the mechanism of PVDF membrane formation was governed by the kinetic factor, i.e. the mutual diffusivity between solvent and non-solvent, rather than their thermodynamic properties.

Yeow et al. demonstrated that different types of solvents during casting PVDF flat sheet membranes could result in the formation of different membrane structures, as shown in Fig. 3 [75]. By using TEP as a solvent, a uniform sponge symmetric structure could be observed throughout the membrane cross-section using water as a coagulant. Similar observations have been previously reported by Bottino et al. [66] and Shih et al. [65]. The authors (Yeow et al.) explained that the resultant membrane structure is attributed to the relatively weak solvent power of TEP in comparison with NMP, DMAc and DMF, which had allowed the minority presence of a non-solvent to induce phase inversion, thus resulted in the occurrence of liquid–liquid phase separation at an early stage [75]. It was also believed that the mutual affinity between TEP and water is relatively weak compared to the other examined solvents, thus favouring the formation of sponge-like membrane structure.

The effects of four different mixed solvents [TMP-DMAc, TEP-DMAc, tricresyl phosphate (TCP)-DMAc and tri-*n*-butyl phosphate (TBP)-DMAc] and different types of PVDF on membrane morphology and performance were systematically investigated by Li et al. [76]. Their results showed that the stronger solvent power of TMP-DMAc and TEP-DMAc resulted in faster precipitation rate and less membrane shrinkage, and consequently higher water flux. The membrane cast from the latter system showed much shorter macrovoids beneath the skin layer, thus contributing to the higher rejection and much better mechanical properties in comparison to the former system.

3.1.1.2. Effect of evaporation time. Munari et al. investigated the effect of evaporation time during casting PVDF flat sheet membranes from various polymer–solvent systems [12]. DMF and NMP were employed as high boiling point solvents, with or without acetone or THF as the low boiling point co-solvents. They found that the morphology and properties of the membranes made from binary solutions containing high boiling point solvents were not signifi-

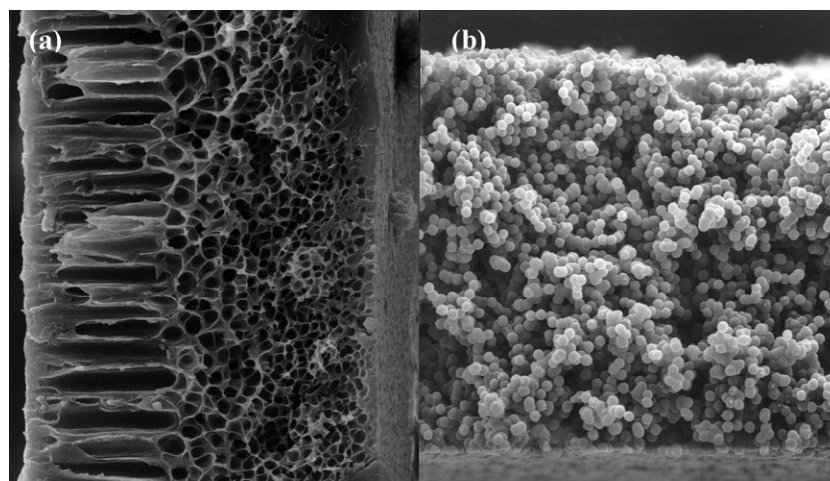


Fig. 4. Cross section images of PVDF membrane with (a) water and (b) 1-octanol as coagulation bath [77].

cantly affected by the evaporation time. However, the evaporation period had influenced the structure of the membranes prepared from ternary solutions containing DMF or NMP and acetone or THF as co-solvents, although their mechanical properties and performance could be changed by the extended evaporation period as a result of precipitation phenomena.

3.1.1.3. Effect of coagulation bath medium. As a semi-crystalline polymer, PVDF membrane formation during phase inversion process is governed by two mechanisms, namely liquid–liquid demixing and crystallisation. Coagulation medium is one of the key elements in determining the sequence of liquid–liquid demixing or crystallisation of the formation of PVDF membrane produced via immersion precipitation process. It is well known that water acts as the strong non-solvent, thus the presence of water as the coagulation medium during immersion precipitation often leads to rapid liquid–liquid demixing process and consequently, membranes with asymmetric structure consisting finger-like voids could be formed [62]. Meanwhile, the employment of solvent in the coagulation bath or the addition of solvent into a water bath may induce delayed liquid–liquid demixing of a polymer and eventually results in the formation of membranes with sponge-like structure. This section describes the effect of different coagulation medium on two main membrane configurations, i.e. flat sheet and hollow fibre PVDF membranes.

Several studies have been performed to investigate the effect of 1-octanol as coagulation bath on PVDF flat sheet membrane formation during immersion precipitation [36,77,78]. Different membrane structures were obtained as shown in Fig. 4 by using two different coagulants. With water (referred as harsh non-solvent) as the coagulation bath, an asymmetric structure consists of dense skin layer accompanied by finger-like structure could be formed during casting of membrane from PVDF-DMF system [77]. However, by substituting water with 1-octanol (referred to as soft non-solvent), the formation of symmetric PVDF membrane comprised of uniform cross-section, packed with almost identical spherical particles was obtained from similar system. The latter structure could be represented by the crystallisation-dominated precipitation, for which crystallisation has preceded liquid–liquid demixing during membrane formation due to the presence of 1-octanol. By varying the compositions of the dopes containing 1-octanol, a wide range of spherulitic particles sizes could be obtained in the prepared membranes [36].

Unlike flat sheet membranes, the mechanism of hollow fibre membrane formation is more complicated as there are more

parameters involved during the preparation of hollow fibre membrane. Hollow fibre membrane is primarily associated with the spinning process, whereby a number of parameters affect the mechanism of membrane formation. For instance, during the preparation of flat sheet membrane, only one ingredient of the coagulation bath is involved, but one has to consider both internal and external coagulation baths during hollow fibre spinning.

Several investigations have been carried out on the effect of internal and external coagulation bath mediums on the properties of PVDF hollow fibre membranes. For instance, the effect of ethanol containing coagulation bath on PVDF hollow fibre membrane morphology was studied by Deshmukh and Li [79]. They observed the structural change of PVDF membranes corresponding to the ratio of ethanol in water in the external coagulation bath. As the ethanol concentration in coagulation bath is increased, the membrane effective porosity and the rate of precipitation decreases leading to a gradual change in the morphology of the membrane outer wall from finger-like structures to sponge-like structures. Based on their studies, the kinetic process is the controlling parameter in the mechanism of membrane formation instead of the relationship of the thermodynamic properties. Similar trends of the membrane effective porosity were observed by Khayet et al. when ethanol is used either in bore liquid or in the coagulation bath or both [80].

On the other hand, Wang et al. obtained the larger effective porosity of PVDF hollow fibre membranes spun from the dope solution containing a high molecular weight additive using ethanol as the bore liquid, rather than the ones prepared by water as the bore liquid [72]. The internal skin of the spun hollow fibre was eliminated by the presence of ethanol as the internal coagulant yielded a relatively higher water flux compared to water coagulant. Ethanol is a weak non-solvent for PVDF, thus the employment of ethanol as the coagulation medium reduces the rate of polymer precipitation.

3.1.1.4. Effect of coagulation bath temperature. Precipitation temperature is one of the factors determining the ultimate membrane morphology and crystallinity of PVDF membranes. As described previously (Section 2.1), a high temperature usually results in the formation of a PVDF membrane with finger-like structures while a low temperature leads to sponge-like structures and/or particulates (if crystallisation occurs). Cheng studied the effect of coagulation bath temperatures on PVDF membrane morphology [34]. By changing the coagulation bath temperature from 25 °C to 65 °C, the morphology of PVDF membranes changed from a symmetric structure composed of spherical crystallites, to an asym-

metric one with dense top surface accompanied by a cellular structure mixed with spherical particles. The former morphology could be described by the occurrence of crystallisation-dominated precipitation, while the latter is attributed to the liquid–liquid demixing. A similar conclusion was drawn by Yeow et al. [75] and Wang et al. [81] on their studies of the effect of coagulation bath temperatures on morphology of PVDF membranes.

3.1.1.5. Effect of non-solvent additives. The addition of a non-solvent additive in the membrane casting solution is one of the methods to improve the membrane morphology, and to enhance the membrane separation as well as the performance. An additive can function as a pore former, increase solution viscosity or accelerate the phase inversion process, whereby one or all the above objectives could be achieved by any of these functions. The type of additives used in the fabrication of PVDF membranes could be divided into three categories: (a) low molecular weight additives, (b) high molecular weight additives or known as polymeric additives, and (c) other types of additives. This section describes the effects of various additives on the resultant PVDF membrane morphology and properties.

(a) Low molecular weight additives: Low molecular weight inorganic salts have attracted much attention as a pore forming additive in the preparation of PVDF membranes. For example, the influence of lithium chloride (LiCl) in the formation of PVDF flat sheet membrane was investigated by Bottino et al. [64]. The addition of LiCl in the casting solution had remarkably changed the morphology of the PVDF membrane, where the formation of porous structure and larger cavities could be observed and these effects were enhanced with higher LiCl concentrations. Because of the high tendency of LiCl to dissolve in water, the precipitation rate of the polymer from dope solution upon immersion process becomes relatively higher. Although there is an observed reduction in the mechanical strength, the water flux is significantly increased without causing an obvious drop in dextran rejection. Similar results were obtained by Tomaszewska in the preparation of PVDF flat sheet membranes for membrane distillation [71]. By increasing LiCl concentrations in dope solution, larger cavities were formed and resulted in the increase of porosity and maximum pore size, while the mechanical strength was drastically reduced which is in agreement with Bottino's work [64].

Meanwhile, the PVDF hollow fibre membranes obtained by Wang et al. exhibited good mechanical strength and high permeate flux with the use of LiCl/non-solvent mixture in the dope solution [82]. Interconnected, a sponge-like structure was observed in the hollow fibre prepared from LiCl/water as the additive, while circular nodules appeared in the membrane prepared from LiCl/1-propanol as an additive. Several other studies have also reported the effect of the addition of LiCl in a dope solution as a pore forming agent or hydrophilic additive during the preparation of PVDF membranes [83,84].

Kong and Li observed a non-linear increase in the dope solution viscosity corresponding to the added amount of LiCl and rapid increase in solution viscosity with NMP as the solvent compared to DMAc [83]. When the concentration of LiCl as the hydrophilic additive is increased up to a certain value, macrovoids formation in PVDF membrane was reduced as observed by Fontananova et al. [84]. Based on their study, the competition between thermodynamic and kinetic effect of the additive in phase inversion immersion precipitation process could be employed to explain the observed phenomenon. At low LiCl concentrations, LiCl acts as a permeate flux enhancer due to the thermodynamic effect and induces the enhancement of liquid–liquid demixing, while at higher concentrations, it suppresses the macrovoid formation as a result of the kinetic effect which induces a delayed demixing process.

Another type of low molecular weight inorganic salt, lithium perchlorate (LiClO_4), was also found to be employed as an additive to improve PVDF membrane properties. Lin et al. determined the quaternary phase diagram of LiClO_4 /water/DMAc/PVDF system and found that the gelation line shifted up progressively with increasing salt concentrations in the system [85]. At a low LiClO_4 content, porous membranes were obtained; however the formation of larger macrovoids in the PVDF membrane structure was observed when the membrane is cast from high salt-containing dope. Yeow et al. investigated the effect of LiClO_4 on the morphology of the resulting PVDF flat sheet membrane [75]. Due to the strong effect of the Li salt on the polymer solution, a membrane with an irregular structure was formed at 2 wt% LiCl. Further to that, they prepared the PVDF membrane in a hollow fibre configuration with the addition of LiClO_4 in spinning solution [86]. Their result revealed that a significant increase in solution viscosity, in line with the raise in the LiClO_4 concentration, is due to the strong interaction between LiClO_4 and solvent DMAc in the dope solution. In addition, at a relatively lower LiClO_4 content, an increase in the mean pore size and more uniform pore size distribution could be obtained, though an excessive additive amount may cause adverse effects.

(b) High molecular weight additives or polymeric additives: Polyvinylpyrrolidone (PVP) is among the most commonly used and studied additives in membrane fabrication as an efficient method to produce highly porous membranes. PVP is hydrophilic in nature, thus the presence of this polymer could enhance the liquid–liquid demixing process during precipitation of the dope solution since they are miscible with water.

Due to its hydrophilic nature, the addition of PVP promotes the non-solvent influx upon immersion in the coagulation bath, thus favouring the formation of large finger-like macrovoids in PVDF hollow fibre membranes [72,79,83]. A significant increase in the effective porosity of PVDF hollow fibre membrane, with membrane mean pore size, remained fairly consistent as observed by Kong and Li when PVP is used as an additive [83]. Similar results were obtained by Wang et al. and Fontananova et al. in their studies on the influence of PVP addition on PVDF membranes [72,84].

The detailed effect of different molecular weights and concentrations of PVP as an additive on the morphology and performance of hollow fibre membrane was further investigated by Wang et al. [72]. Low molecular weight of PVP (M_w : 10,000) results in a membrane with high water flux and good solute retention, while opposite effects could be observed on the membrane prepared with higher molecular weight PVP (M_w : 360,000). While low molecular weight PVP tends to create small pores and easily leaches out from the membrane, most of the high molecular weight PVP remains in the membrane and may block the path of the interconnected voids. Morphology of the hollow fibre prepared from the former exhibits two layers on the fibre wall and big cavities in the inner layer, while the inner layer cavities which are reduced with no clear boundaries between these two walls, could be observed on the membrane prepared from the latter. Their experimental results indicate that increasing PVP concentration causes water flux decrease and high rejection.

Another type of polymeric additive, poly(ethylene glycol) (PEG), has been reported to improve the pure water flux of membranes with a relatively lower rejection rate, the effect of which could be reversed by heat treatment longer than 10 min [11]. Uragami et al. explained the latter phenomenon based on membrane shrinkage behaviour after treatment [11].

(c) Other types of additives: The employment of glycerol as a non-solvent additive for different solvent systems has been reported by Shih et al. [65]. For the case where TEP was used as a solvent, an increase in the mean pore size and effective porosity of the prepared membrane were observed with increasing glycerol concentration, due to the formation of a thin skin layer. On the contrary, increas-