

Table 5

Properties of PVDF hollow fibre membranes and their preparation conditions [73].

Dope solution composition (wt%)	External composition (wt%)	OD/ID (μm)	Porosity (%)	Tensile strength (MPa)	Elongation at break (%)
PVDF/NMP 15/85	Tap water	680/400	82.3	2.78	65.3
PVDF/NMP 15/85	Water/methanol, 50/50	740/400	79.1	2.81	69.57
PVDF/NMP 15/85	Water/ethanol, 50/50	790/400	78.8	2.6	56.8
PVDF/NMP 15/85	Water/isopropanol, 50/50	780/400	79.1	2.19	55.89
PVDF/NMP 17/83	Tap water	760/400	76.9	2.18	53.41
PVDF/NMP 19/81	Tap water	800/400	73.8	0.85	56.99
PVDF/NMP/water 15/83/2	Tap water	680/360	80.1	2.32	110.51
PVDF/NMP/methanol 15/75/10	Tap water	700/400	79.8	1.37	46.79
PVDF/NMP/ethanol 15/75/10	Tap water	720/380	77.7	0.79	36.51

Other spinning conditions: bore liquid composition: 90% NMP in water; air gap: 10 mm; Spinneret dimension (OD/ID): 1.2/0.8 mm.

ing glycerol concentration resulted in a membrane with increased mean pore size, but decreased effective porosity when DMSO was employed as a solvent. The authors attributed the results to the different affinity of the solvents towards the water coagulation bath.

Meanwhile, the addition of water as an additive in the dope solution has been reported to increase the pore radius and effective porosity of the prepared membrane [87]. Khayet and Matsuura also showed that the mass transfer resistance of the membrane decreases with the increase of water amount. Another type of non-solvent additive, that is 1,2-ethanediol, has been employed by Khayet et al. and resulted in the increase in maximum pore size, hence improving the pure water flux [88]. The membrane porosity was observed to be larger in conjunction with the increase in the maximum pore size, although the effective porosity was found unaffected by the addition of 1,2-ethanediol.

3.1.1.6. Effect of spinning parameters on PVDF hollow fibre membranes. In the recent years, considerable effort has been devoted to the fabrication and applications of PVDF membranes with hollow fibre configuration [79,80,83,89]. Due to its high packing density, hollow fibre is mostly preferred over other configurations in industrial operations. However, it is universally recognised that the formation of hollow fibre membranes is much more complex than that of flat sheet membranes. While some of the information obtained from the casting of flat sheet membranes may be useful in fabricating hollow fibre membranes, similar conditions could not be simply extended to obtain hollow fibre membranes with comparable performance and morphology because phase inversion takes place at both inner and outer surfaces. There are many factors influencing the ultimate membrane morphology and performance of PVDF hollow fibre membranes. In this section, the effect of spinning conditions of PVDF hollow fibre membranes is discussed.

Increasing the distance of air gap, is recognized as a way to affect the outer skin formation of hollow fibre membranes. The water permeation flux of PVDF hollow fibre membranes tends to increase with decreasing air gap, with no significant influence on the dextran rejection due to the formation of a thinner skin layer [72,90]. Hollow fibre membranes with thinner and denser sponge-type cross-sections are formed with increasing air gap length, due to a greater molecular orientation and chain package [90].

The extrusion rate of polymer dope plays an important role in determining the ultimate membrane dimensions, especially the membrane outer diameter and wall thickness. Ren et al. investigated the relationship between the dope shear rate within the spinneret (which corresponds to the polymer extrusion rate) with PVDF membrane morphology and performance [91]. The increase in water permeation flux corresponding to the increase of shear rate could be observed while maintaining an almost similar dextran rejection. The authors explained that the shear induced molecular orientation may have occurred but the orientation degree

was small, which resulted in aggregation or loosely connected molecule-clusters.

Much work has been done by Chung and co-workers associated with the effects of spinning conditions in order to gain better understandings on the formation mechanism of PVDF hollow fibre membranes [73,92–94]. Most of these studies focused on the fabrication of PVDF hollow fibre membranes for membrane distillation purpose. One of the major issues, that often limits the application of PVDF hollow fibre membrane in this area, is the formation of macrovoids in membranes. In general, the formation of macrovoids is undesirable because it is the main cause of the reduction in mechanical properties, which eventually leads to the membrane failure especially under high pressure. Several attempts have been made in preparing macrovoid-free PVDF hollow fibre membranes using a triple-orifice or occasionally referred to as a dual layer spinneret [94,95]. Fully macrovoid-free PVDF hollow fibres with increased surface porosity were formed by applying two-phase flow consisting of a solvent and dope solution in the air gap area using a dual layer spinneret, prior to entering the external coagulation bath [94]. By pumping solvent such as NMP or IPA/water mixture, as the weak external coagulants through the outer channel of the spinneret, the solidification process of PVDF polymer solution could be delayed for porous skin layer formation [95].

The fabrication of PVDF hollow fibre membranes with desirable properties could be achieved by controlling the dope composition, rheology, and coagulant composition, which determine the resultant membrane morphology and mechanical properties [73]. Some of the obtained results from the spinning of PVDF hollow fibre membranes are tabulated in Table 5. Nevertheless, it is important to note that the combined effects of all these parameters will determine the ultimate PVDF membrane morphology, and the corresponding membrane separation performance, as none of these parameters are able to stand independently.

3.1.2. Thermally induced phase separation

Apart from immersion precipitation, thermally induced phase separation (TIPS) is another useful technique for the preparation of polymeric membranes from phase inversion process. In the membrane preparation using the TIPS method, a homogeneous solution is prepared by dissolving a polymer in a high boiling point, low molecular weight diluent at high temperature, the solution is cast into the desired shapes and then cooled to induce phase separation and solidification of the polymer. After that, the diluent is removed to produce a microporous membrane structure. The major parameter that distinguishes between the TIPS and IP is that the former method requires the removal of thermal energy to convert the solution to a two phase mixture, while the latter involves an exchange between non-solvent and solvent for membrane formation.

Much work, related to the preparation of membranes via TIPS from various polymers such as PP and PE has been carried out [96–99]. Preparation of PVDF membranes using TIPS has been recognised since the late 1980s, where a number of PVDF micro-

Table 6Properties of PVDF hollow fibre membranes fabricated from TIPS using SiO₂ particles [100].

Composition (vol%)				OD/ID (mm)	Average pore size (μm)	Max. pore size (μm)	Water flux (L/m ² h bar)	Tensile strength (kg/cm ²)	Tensile elongation at break (%)
PVDF	SiO ₂	DOP	DBP						
31.5	12.2	51	5.3	1.98/1.02	0.94	1.57	8240	121	378
31.7	12.2	45.5	10.6	2.03/1.11	0.26	0.44	2370	73	182
32.3	14.8	48.5	4.4	2.00/1.10	0.59	0.91	7000	115	300

filtration and ultrafiltration membranes have been developed [14,100–103]. However, the emergence in the fabrication of PVDF membranes via TIPS method is observed to be more significant in the recent years [104–110].

In the TIPS process, the selection of a diluent is crucial in determining the polymer crystallisation process and the resulting membrane morphology; hence affecting the membrane properties, such as pore size, strength, flux, etc. For this reason, there has been enormous attention on the effect of diluents on the properties and morphology of PVDF membranes prepared via this process [108–111].

Lloyd et al. employed dibutyl phthalate (DBP) as a diluent for preparation of microporous PVDF membranes via TIPS [103]. Membranes with irregular fuzzy structures were obtained from this study. Meanwhile, Gu et al. observed the formation of different structures of PVDF membranes prepared from different types of diluents [108]. PVDF membranes prepared from dimethyl phthalate (DMP) as diluent, exhibited the most discernable and the largest spherulitic structures compared to that of prepared from DBP, or mixtures of DMP with dioctyl sebacate (DOS) and dioctyl adipate (DOA) as diluents. The authors attributed the morphology differences to the degree of interactions of polymer–diluent that influence the extent of PVDF crystallisation. By using different types of diluents, the crystallisation temperature of PVDF during the TIPS process is also changed. The crystallisation temperature, T_c of PVDF using four different diluents was observed to be in the following order: γ -butyrolactone (γ -BA) < propylene carbonate (PC) < DBP < dibutyl sebacate (KD), as reported by Su et al. [109].

There are two types of TIPS processes: solid–liquid (S–L) separation or liquid–liquid separation with subsequent crystallisation. The major factor determining the type of phase separation that occurs for a system involving a semicrystalline polymer is the miscibility of the system, which is associated with the strength of polymer–diluent interactions [112]. In general, membranes prepared from PVDF–diluent binary mixtures, using TIPS, often undergo solid–liquid phase separation. However, this may not always be true for some systems. For instance, Yang et al. observed the formation of PVDF membranes with bicontinuous structures due to the occurrence of liquid–liquid phase separation when using diphenyl ketone (DPK) as a diluent in polymer–diluent binary mixtures [110].

On the other hand, using mixed diluents in a polymer–diluent system during preparation can also affect the polymer crystallisation and the morphology of membranes. With increasing cyclohexanone (CO) content in the γ -BA/CO diluent mixtures, Su et al. observed structural changes of membrane cross-sections from spherulite-like crystallites to sheaf-like crystallites [113]. Phase diagrams of PVDF/DBP/di(2-ethylhexyl)phthalate (DEHP) ternary blend were determined by Ji et al. as a tool for controlling the morphology and interpreting membrane structure [106]. They observed the increase in the size of spherulites that present in membrane cross-sections with the increase of DBP ratios, which can be explained by the enhancement of the compatibility between PVDF and diluents, yielding to the occurrence of polymer crystallisation before liquid–liquid phase separation. Following that, the aforementioned mixed diluent has been employed in the fabrication of PVDF microporous matrix of polymer electrolyte for lithium

ion batteries [114]. By varying the DBP/DEHP ratios in the mixed diluent, the membrane microstructure was easily and conveniently controlled.

Meanwhile, the structure of the PVDF membrane prepared from DBP (good diluent) gradually changed from a large spherulite morphology to bicontinuous or a uniform porous structure with increasing dioctyl phthalate (DOP, poor diluent) compositions in DBP/DOP mixed diluents, as reported by Li et al. [115]. From the phase diagram, the cloud point curves shifted to higher temperatures with increasing DOP contents in the mixed diluents, thus the liquid–liquid phase separation could be induced via the adjustment of the mixed diluents composition.

The cooling rate and the quenching condition are other factors influencing the extent of crystallisation of PVDF membranes during the TIPS process. From Su et al. observation, the increase of cooling rate decreased the crystallisation temperature of PVDF while promoting the crystallisation [109]. By varying the quenching conditions, PVDF is crystallised in different extents and different crystal phases are formed. Gu et al. obtained α -phase crystals by quenching a PVDF–DMP system to different temperatures above 40 °C, while the β -phase crystal structure was formed when the system was quenched from liquid nitrogen and crystallised for 24 h in 25 °C water bath [116]. On the other hand, the decrease in cooling rate has lead to the formation of larger spherulitic particles and channel sizes of open pores between particles, as reported by Cui et al. based on their study using sulfolane as a diluent [111]. This has resulted in wider pore size distribution and poor mechanical strength of porous membranes.

The introduction of inorganic particles such as CaCO₃ and SiO₂ particles into dope solution is known to be useful in the preparation of membranes with enhanced properties, and the effects of these particles on the morphology and properties of PVDF membranes prepared via TIPS have been investigated [100,104,117]. Li and Lu observed that the presence of CaCO₃ particles hindered the aggregation and the growth of crystal nuclei during polymer crystallisation, therefore the formation of spherulites was disturbed at the quenching condition [117]. Nevertheless, the addition of CaCO₃ particles showed negative effects on membrane tensile strength.

SiO₂ particles were added into PVDF–DBP system to improve the membrane performance [100,104]. Doi and Matsumura described the presence of SiO₂ particles as beneficial for improving the flowability in the moulding process, by controlling the absorbing diluents from being liberated from PVDF resin, while functioning as a nucleus for micro-phase separation between the diluent and PVDF during cooling of the molded membrane [100]. After the formation of membrane, a concentrated sodium hydroxide aqueous solution was used to wash out SiO₂ particles at an elevated temperature. As a result, membranes obtained by this method had a porous symmetric sponge-like structure with excellent performance and excellent mechanical strength. Table 6 lists the properties of PVDF hollow fibre membranes fabricated from TIPS using SiO₂ particles.

However, PVDF has poor stability in caustic environments (as previously mentioned in Sections 2.2 and 2.3), where the degradation of PVDF membranes has been observed at the exposure to high concentrations of caustic, which had caused in the reduction of membrane mechanical strength [46,54]. Therefore, careful consideration should be taken when using the concentrated sodium

hydroxide solution for washing out SiO₂ particles particularly at higher temperature.

Matsuyama and co-workers employed glycerol triacetate (triacetin) and glycerol as the respective solvent and non-solvent, in the preparation of porous PVDF hollow fibre membrane for the application of water treatment [105]. It was observed that the mechanism of membrane structural formation changed from polymer crystallisation to liquid–liquid phase separation as a result of a non-solvent addition. Two kinds of membrane structures were formed, i.e. interconnected and spherulite structure with PVDF/triacetin/glycerol system. The addition of glycerol to the dope solution was found to be effective in preparing membranes with higher water permeabilities, provided the air gap distance was short and temperature of the polymer extrusion was low. Following that, they prepared hollow fibre membranes for CO₂ absorption by adding PEG or glycerol to the dope solution [118]. Seven kinds of asymmetric PVDF hollow fibre membranes with considerable different structures at the outer surface were prepared via TIPS and their feasibility studies for CO₂ absorption were investigated. The performances of the PVDF membranes were found to be comparable with that of the commercial PTFE membrane.

The effect of liquid paraffin as a bore liquid during the preparation of PVDF hollow fibre membranes via TIPS has been investigated by Ji et al. [119]. Liquid paraffin is a non-solvent for PVDF but a solvent for diluent mixtures of DBP/DEHP. The structure of inner surface for hollow fibre membrane prepared from PVDF/DBP/DEHP system was observed to be affected by the exchange between bore liquid and a diluent mixture. The hollow fibre membrane with porous inner and outer surfaces and interconnected cross-sectional structure was obtained from their study.

3.2. Use of inorganic particles

In the recent years, the addition of inorganic particles with polymer solutions has become as one of the attractive methods in the fabrication of polymeric membranes [61,120–122]. Most of the research work has focused on the preparation of composite or hybrid organic–inorganic membranes by the incorporation of inorganic particles to modify the membrane properties for various purposes. For instance, the presence of the dispersed inorganic particles in the membrane matrix has been reported to improve the membrane performance and properties particularly by:

- (1) enhancing mass transfer in membrane pervaporation process [123]
- (2) increasing selectivity in gas separation [124]
- (3) improving membranes hydrophilicity and fouling resistance properties [120,125]
- (4) improving the mechanical properties [60].

Inorganic particles that have been incorporated into PVDF membranes include TiO₂ [120,125], Al₂O₃ [121,126], ZrO₂ [122] and SiO₂ [61,127,128]. The fouling resistance properties of PVDF membranes have been improved by incorporating TiO₂ or Al₂O₃ into polymer solutions to form PVDF membranes [120,121,129]. The presence of TiO₂ particles as an inorganic fillers in PVDF membrane has resulted in the improvement of mechanical resistance at an elevated pressure and temperature compared to pure PVDF membrane [60].

Recently, considerable effort has been devoted to investigate the effect of SiO₂ particles on PVDF membrane performance [127,128,130]. Bottino et al. explained that a drastic increase in the solution viscosity caused by the increasing SiO₂ amount was attributed to the strong interactions between the solvent (NMP) and the silanol groups [61]. Because SiO₂ possesses comparable chemical resistance and good compatibility with the organic solvent used to prepare PVDF solutions, it has been employed in

the preparation of PVDF membranes for ultrafiltration purposes [61]. The hydrophilic properties of PVDF ultrafiltration and anion-exchange membranes were also improved by the incorporation of SiO₂ particles into the membrane [127,128]. The example of PVDF hollow fibre microfiltration membranes with excellent performance and good mechanical strength, achieved using SiO₂ as inorganic particle additives can be seen from Table 6 in the previous section. Hashim et al. employed SiO₂ particles in the preparation of PVDF hollow fibre membranes from the conventional immersion precipitation technique, and removed the particles out from the formed membranes by a treatment using either NaOH solution or hydrofluoric (HF) acid [131]. Both acid and alkali treatments resulted in PVDF membranes with a remarkably higher water flux. HF acid treatment did not affect the mechanical strength of PVDF membranes, however, the membranes treated with NaOH solution might have undergone degradation due to the chemical attack caused by the NaOH.

However, since this is still a relatively new topic, the detailed mechanisms of how inorganic particles influence the membrane formation particularly during phase inversion process remain unclear.

3.3. Sintering

Sintering is widely used in the commercial production of inorganic membranes, as well as symmetric PTFE and PP membranes due to the low solubility to solvents. This method involves the compression of powder containing particles of a given size and sintered at elevated temperatures. Nevertheless, there were two patents reported by Glasrock Products Inc. and Solvay & Cie on the preparation of porous PVDF membranes via sintering method [58,59]. PVDF powder was dispersed in methyl isobutyl ketone (MIBK) and the dispersion was broken into droplets. A porous PVDF structure was subsequently obtained by sintering the droplets at certain temperatures [58]. Meanwhile, cellular or dense structures were obtained by the extrusion of a moulding composition containing PVDF Solef polymer and chemical blowing agent [59].

3.4. Track etching

Occasionally, track etching, is used for the fabrication of PVDF membranes [47,57]. In the track etching method, polymer film or foil is subjected to high energy particle radiation (metal ions) applied perpendicular to the material, followed by etching in acid or an alkaline bath [63]. Consequently, cylindrically shaped pores with uniform pore size distributions could be obtained. While the membrane porosity is mainly determined by the duration of radiation, the pore size is determined by the etching time and temperature. Komaki observed the growth of fine holes in PVDF film exposed to fission fragments of oxygen and etched in sodium hydroxide solutions by gas-flow method and electron microscopy [47]. In the recent study performed by Grasselli and Betz [57], membranes with a pore diameter in the range of few hundred nanometers were obtained by the irradiation of PVDF film with heavy ions beam of Sn which then exposed to several etching conditions involving permanganate oxidation.

3.5. Other methods

Phase separation using supercritical CO₂ as non-solvent is an emerging method in the preparation of PVDF membranes. This method can be considered as environmental friendly because the solvent initially exist in polymer solution could be easily recovered in the supercritical CO₂ phase after the exchange of solvent and CO₂. Moreover, membranes could be dried directly without collapsing the pore structures due to the absence of a liquid–vapour interface

[132]. Cao et al. reported the preparation of porous poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) membranes from phase separation with the supercritical CO₂ as non-solvent [133]. Dry membranes with sponge-like and asymmetric structure were obtained from PVDF-HFP/acetone system by varying the experimental conditions such as CO₂ pressure, polymer concentration and temperature. Following that, Huang et al. prepared microporous PVDF membranes from the PVDF/DMAc system by using the supercritical CO₂ phase inversion process [132]. The resulting membranes exhibited morphological characteristics from both liquid–liquid demixing and crystallisation, whereby the membrane structure with cellular porous surrounded by interlinked PVDF particulate crystallites was formed. Although membranes prepared via this method showed porous and macrovoid-free structure, the obtained membrane pore size can be considered as relatively large, which was between 1 and 10 μm [133].

Electrospinning is a feasible technique to produce sub-micro to nano-scale fibres through an electrically charged jet of polymer solution/melt. Electrospun nanofibrous membranes possess several attractive attributes such as high porosity, pore sizes ranging from nanometers to micrometers, interconnected open pore structures, high permeability, large surface area per unit volume and tailorable membrane thickness. In a typical production process of electrospun PVDF membranes, a pendant droplet of PVDF solution at the capillary tip is deformed into a conical shape under the electrostatic field. When the electrostatic forces overcome the surface tension, a charged jet is ejected. The jet was deposited on a support and collected in a form of non-woven hybrid membrane, which can be used in the fields of ultrafiltration, microfiltration, nanofiltration, air filters and electrolytes [134–137].

A number of methods have been studied and employed for the preparation of PVDF membranes in either flat sheet or hollow fibre configurations. Method selection is highly dependent on the application of PVDF membranes as well as research interests. From the separation point of view, the first task would be the control of membrane pore size. Generally, membranes produced via different methods exhibit different properties of pore sizes and porosities [63].

4. Hydrophilic modification of PVDF membrane

PVDF is a semi-crystalline polymer with a glass transition temperature (T_g) of around -39°C , a melting temperature (T_m) of around 160°C and a thermal decomposition temperature of above 316°C . The macromolecular linear chain structure of PVDF is $-\text{CH}_2\text{CF}_2-$, in which the bond energy of C–F, C–H and C–C is 453, 414.5 and 347.5 kJ/mol respectively. The $-\text{C}-\text{C}-$ bond of the main polymer chain is surrounded by fluorine and hydrogen atoms, resulting in excellent chemical, thermal and mechanical stabilities. PVDF can be dissolved in some polar solvents, such as DMAc, NMP, DMSO, and DMF, due to the polar property derived from the alternative arrangement of $-\text{CF}_2-$ and $-\text{CH}_2-$ groups, which makes it an ideal membrane material for the preparation of PVDF membranes using the non-solvent induced phase inversion method. However, there are still some problems for PVDF membranes which limit the further developments and applications of PVDF membranes especially in the areas of purification and separation of aqueous solution systems such as drinking water production, wastewater treatment, bio-separation. The critical problems lie in:

- (1) The surface energy of PVDF, which is very low, and the critical surface tension (γ_c) of PVDF, $-\text{CF}_2-$ and $-\text{CH}_2-$, which are 25 mN/m, 18 mN/m, and $\gamma_c = 31$ mN/m respectively. This results in the poor wettability of the PVDF membrane. Therefore, the

pure water flux is usually low due to the strong hydrophobic nature of PVDF.

- (2) The hydrophobic PVDF membrane is susceptible to fouling while treating aqueous solution containing natural organic matters, e.g. proteins. Proteins are prone to be easily absorbed onto the membrane surface or block the surface pores, decreasing the permeability and the final separation performance, depressing the lifetime of the membranes and subsequently causing more operation costs of the replacement and maintenance of the membrane modules.

One major possible reason for the protein fouling on the hydrophobic PVDF membrane is that there are almost no hydrogen bonding interactions in the boundary layer between the PVDF membrane interface and water. The repulsion of water molecules away from hydrophobic PVDF membrane surface is a spontaneous process with an entropy increasing and therefore protein molecules have a tendency to adsorb onto membrane surface and dominate the boundary layer. In contrast, the membrane with the hydrophilic layer possesses a high surface tension and is able to form the hydrogen bonds with surrounding water molecules to reconstruct a thin water boundary between the membrane and bulk solutions. It is difficult for hydrophobic solutes, like some proteins, to approach the water boundary and break the orderly structure because an increase of energy would be required to remove the water boundary and expose the PVDF membrane surface.

Besides the hydrophilicity/hydrophobicity effect of the membrane, the charge and ionic strength of membranes, morphological properties of porous membranes including surface roughness, pore size distribution, porosity, tortuosity and thickness, the properties of the solutes, the mode of flow, membrane configuration also have an undeniable influence on the membrane fouling; however, the emphasis of this review would be placed on the hydrophilic modification as most of the studies have been conducted to modify the intrinsic properties of PVDF membranes.

Therefore it is very significant to improve the hydrophilicity of PVDF membranes through versatile methods to enhance the lifetime and reduce the operation cost of the PVDF membrane module. Different modification ways have been explored to tailor the surface engineering of the PVDF membrane in recent years. Two straightforward ways are usually used to catalogue the diverse hydrophilic and fouling resistant modification techniques, which can be mainly classified into surface modification and blending modification. Surface modification is usually achieved by coating or grafting a functional layer on the prepared membrane surface, in which most of the modified sites occurred on the top and/or bottom surface of the membrane, excluding the pores inside the membrane, due to the limited diffusion ability of the modifying agents into the membrane pores. Blending modification is usually used to achieve the desired functional properties along with the membrane preparation, therefore the preparation and modification process can be accomplished in a single step. Both the surfaces and inside-pores of the membrane have a window of opportunity to be modified synchronously through the synergy effect between PVDF and compatible additives.

4.1. Surface modification of PVDF membrane

Surface modification of PVDF membranes can be classified into two categories: surface coating and surface grafting. Surface coating is the simplest way to improve the surface hydrophilicity of the PVDF membranes temporarily through coating or depositing a thin functional hydrophilic layer onto the membrane surface. The main problem of the surface coating is the instability of the coated layer, which could be washed away along the operation and cleaning process because of the relatively weak physical adsorption interaction

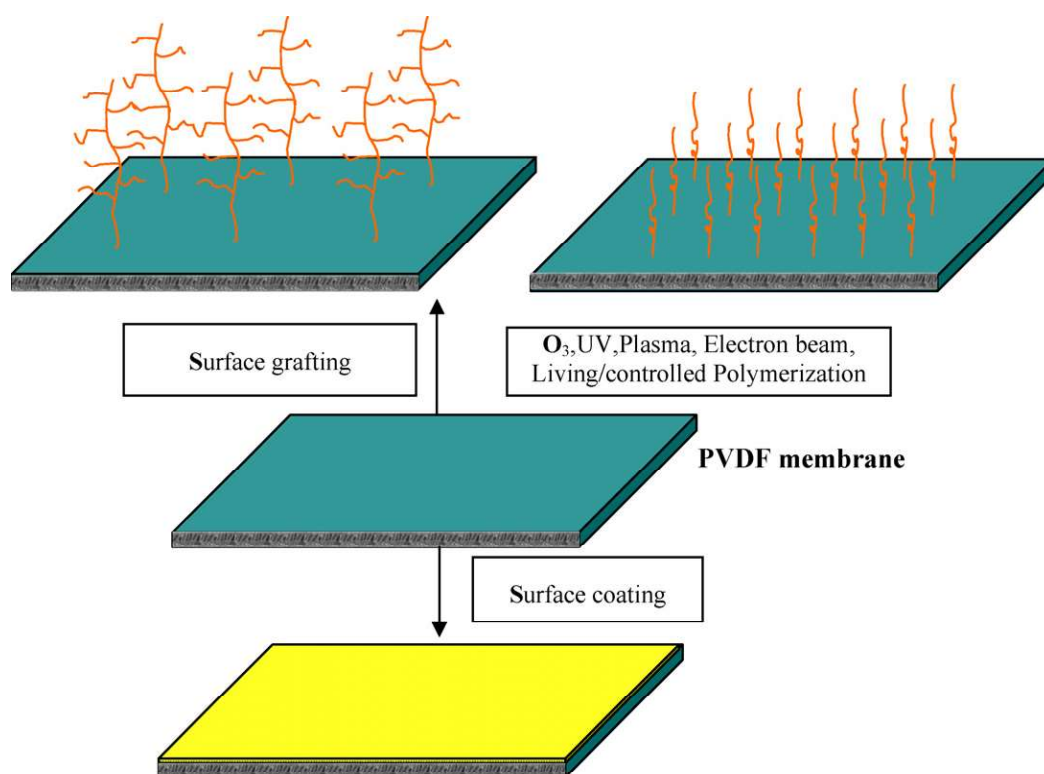


Fig. 5. Schematic of surface modification of PVDF membrane.

between PVDF membrane and coated layer. In some cases, chemical treatments such as sulfonation or crosslinking were performed on the membrane surface to anchor the coated layer, while surface grafting can conquer the instable problem completely by the grafting polymerisation of monomers, which immobilises the functional chains, brushes or layers onto the membrane surface through covalent bonding interaction. Fig. 5 illustrates the route of surface modification including surface coating and surface grafting.

4.1.1. Surface coating

A hydrophilic layer can be simply coated on the hydrophobic PVDF membrane surface to enhance both hydrophilicity and fouling resistance. The binding between coated layer and PVDF membrane can be implemented through physical adsorption, crosslinking, and sulfonation. In most surface coating cases, glycerol was coated on the PVDF membrane surface to keep the wettability of membrane temporarily during the transportation and storage. However, the glycerol layer was usually washed away before operation. In other case, the PVDF membrane surface was dipped with an aqueous solution containing 0.2–1.5% cellulosic polymer, 0.5–5% low M_W co-reactant (amines/hydroxy comp.), 1–3% additives (surfactants, cross-linking agents, etc.), and then the hydrophilic components were bound to the membrane surface by an addition reaction (the curing step). Therefore the hydrophilic properties with the contact angle as low as 42° were imparted to the hydrophobic PVDF ultrafiltration membranes, and some of these membranes are now commercially available and supplied by DDS FILTRATION, designated ETNA series [138,139]. The PVDF membrane can also be modified by a surface coating with a dilute poly(vinyl alcohol) (PVA) aqueous solution followed by solid–vapor interfacial cross linking. The increase of hydrophilicity resulted in a comparable pure water permeability compared to the unmodified membranes [140].

Another important factor which affects the fouling properties of PVDF membrane is the surface charge and ionic strength of mem-

brane while treating the charged foulants, which is often the case. Usually, it is appropriate to use a membrane carrying the same electrical charge as the foulants. Therefore, negatively charged PVDF microfiltration membranes were prepared using direct sulfonation with chlorosulfonic acid [141]. Negative charges ascribed from hydroxyl ($-\text{OH}$) and sulfonyl groups ($-\text{SO}_3$) were incorporated on the surface of the membrane. Such modified membranes can have molecular weight cut-off (MWCO) about five times smaller than the size of the solutes because of the electrostatic repulsion.

However, the modified membrane with small hydrophilic groups like hydroxyl ($-\text{OH}$) and sulfonyl groups ($-\text{SO}_3$) might not be chemically stable, which could be oxidised in the air. In addition, the intense sulfonation could affect the bulk and surface microstructure of the PVDF membrane and cause the dramatic decrease of mechanical strength.

Other hydrophilic macromolecules such as PVP bearing the structure of lactam, which makes PVP groups interacting with hydroxyl groups of the hydrophilic PVDF membrane due to the hydrogen bonding effect and can be further introduced to the PVDF membrane surface after an alkaline modification. The modified membrane is promising and practical to further purify flavonoids from crude Ginkgo biloba extraction (GBE) products [142]. Although, most of surface coating cases focused on the membrane surface, Boributh et al. coated the PVDF membrane with chitosan solution, through the combined flow through and surface flow method, which allowed the chitosan molecules to be coated both on the membrane surface and pore walls [143]. Modified membranes exhibited good anti-fouling properties of reducing the irreversible membrane fouling. Different surface coating approaches are listed in Table 7 [138,140–145].

Most of the methods would cause the decrease of the pure water flux because of the unavoidable accumulation of the coated layer on the pore surface although the hydrophilicity and fouling resistance could be improved to some extent.

Table 7
Properties and performances of PVDF membrane modified by surface coating.

Surface coating	PVDF membrane	Pure water flux (L/m ² h)	MWCO (Da)	Water flux recovery	Contact angle (°)	Coated layer
Original	FS50-U	300–500 (2 bar)	50,000			Cellulosic polymer, co-reactant (amines/hydroxy comp.), additives (surfactants, cross-linking agents, etc.) [138]
Modified	ETNA 20A	200–300 (4 bar)	20,000	97%	42	
Original	HFP-707(Koch)	930 (1 bar)	120,000		81 ± 1	Poly(vinyl alcohol) (PVA) [140]
Modified	PVDF/PVA membrane	830 (1 bar)		95% ^a	68 ± 1	
Original	PVDF 0.22 μm, Millipore	246 (1.4 bar)		0.4 ^d	91	Sulfonation [141]
Modified	SPVDF	19,000 (1.4 bar)	90% ^c	0.65 ^d	66	
Original	PVDF	133.3 (3 bar)	97% ^b			Sulfonation [144]
Modified	SPVDF	162.5 (3 bar)	93% ^b			
Original	Shanghai Xinya	140 L/m ² h MPa	6000			PVP [142]
Modified	PVDF/PVP	290 L/m ² h MPa				
Original	PVDF 0.2 μm				97.4 ± 3.6	3,4-Dihydroxyphenylalanine
Modified	PVDF/poly(DOPA)				53.6 ± 2.8	(DOPA) [145]
Original	PVDF 0.22 μm, Millipore	1510 (1.5 bar)	50,000	8–10%	115 ± 2	Chitosan [143]
Modified	PVDF/Chitosan	972–247 (1.5 bar)	>162,000	45–57%	73–61.5	

^a Water flux of modified membrane is 95% higher than original membrane after 18 h Grand River water flux filtration.^b Rejection of human albumin.^c Monodisperse poly(styrene sulfonic acid), sodium salt MW 500,000 (Polysciences Inc.). PSSA, with an approximate root mean square radius of 40.5 nm.^d Normalized flux, J/J_0 , J is the fouling flux of solution (100 mg/l PSSA); J_0 is the steady state water flux at 1000 LMH.

4.1.2. Surface grafting

Surface grafting is one of the most promising methods to modify the membrane surface through the covalent bonding interaction between the grafted chains and the membrane. Covalent attachment of graft chains on the membrane surface avoids their delamination and offers a long-term chemical stability of grafted chains, in contrast with physically surface coating method [146]. Surface grafting can be achieved by versatile means (e.g. UV photo irradiation, plasma, high energy irradiation and “living”/controlled polymerisation). According to different types of monomers, surface grafting can also be classified into two categories: grafting with a single monomer and grafting with a mixture of two (or more) monomers [147].

The first type usually occurs in a single step, but the second may occur with either the simultaneous or sequential use of the two monomers. The medium where the surface grafting happens can also be classified into aqueous medium and organic solvent. Not only monomers can be polymerized onto the membrane surface through a different initiation process, which is usually considered as “grafting from”, but also polymers can be directly immobilised on the membrane surface through coupling reaction, which is considered as the “grafting to” [146,148,149].

“Grafting to” methods have the potential advantage that the graft polymer can be well synthesised and characterised in details before grafting. However, the grafting degree on the membrane surface might be limited due to the well-known low reactivity of the coupling reaction, which is not straightforward enough for industrial applications despite the precise control of graft chain structure.

“Grafting from” has much more choices to control the grafting degree, chain lengths and structure by varying different initiating means, monomer, concentration, temperature, solvent, additive, and other reaction conditions. In order to achieve the ultimate aim of modifying the PVDF membrane with improved functions, a synergy between the excellent intrinsic properties of the PVDF membrane (e.g. mechanical strength, chemical and thermal stability) and the novel functional grafted layer (e.g. hydrophilicity and fouling resistance) must be comprehensively considered. In this review, “Grafting from” will be reviewed based on different initiating means. All versatile ways to modify the PVDF membrane surface and all other properties of the modified membrane are listed in Table 8 [19,150–163].

4.1.2.1. UV. PVDF has a very good resistance to UV photo radiation (the wavelength ranges in 100–400 nm) because no significant changes were detected either at a molecular level or in the electro-active response. It is difficult to directly activate the PVDF membrane surface through UV radiation due to its less electroactive property [164]. However, the photo-initiator benzophenone was usually needed to initiate the photo grafting polymerisation process on the PVDF membrane surface. Benzophenone was decomposed to starter radicals from the cleavage of a weak bond in benzophenone, and then the starter radicals transferred to the PVDF membrane and abstract hydrogen atom from surrounding chemical species, which led to the generation of initiating radicals. Benzophenone can be coated onto the membrane surface by dipping the membrane in benzophenone solution, which can be considered as an adsorption method. This method could minimize the homopolymerisation of monomer and enhance the grafting efficiency [150,165,166]. Both monomer concentration and polymerisation time influenced the grafting degree. PVDF microfiltration membranes were modified by 2-dimethylaminoethylmethacrylate (qDMAEM) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) using benzophenone as the photo-initiator to demonstrate a strong antimicrobial action to the *Escherichia coli* bacteria [165].

Rahimpour et al. performed the UV photo-grafting modification on the PVDF membrane with hydrophilic acrylic and amino

Table 8
Properties and performance of PVDF membranes modified by surface grafting.

Surface grafting	PVDF membrane	Pure water flux (L/m ² h)	MWCO	Water flux recovery	Contact angle (°)	Monomer
Original	PVDF	359 (50 psi)	93% ^b	24%	92.3	Acrylic acid (AA) and 2-hydroxyethylmethacrylate (HEMA),
Modified		124–333 (50 psi)	95–98% ^b	31–62%	66–82.7	2,4-phenylenediamine (PDA) and ethylene diamine (EDA), UV [150]
Original	PVDF	946 (42 kPa)	0.193 μm ^a	32.8%	86	N-vinyl-2-pyrrolidinone (NVP), UV
Modified	PVDF-g-PVP	135 (42 kPa)	0.073 μm ^a	83–93%	32	[151]
Original	ENM, HVHP		3.58, 1 μm ^c		132 ± 9, 124 ± 8	Methacrylic acid (MAA), plasma
Modified	Grafted ENM, HVLP		0.88, 0.9 μm ^c		62, 67	[152]
Original	PVDF 0.65 μm, Millipore	14,220 (0.2 bar)	50,000		115 ± 2	Poly(ethylene glycol) (PEG),
Modified	PVDF-g-PEG	9720 (0.2 bar)	>162,000		73–61.5	plasma [153]
Original	PVDF	578 (0.1 MPa)	73% ^d		82	Styrene, plasma [154]
Modified	PVDF-g-poly(styrene)	23 (0.1 MPa)	96% ^d		110	
Original	PF45	5 (1 bar)	40% ^e		90	Ar and NH ₃ plasma [155]
Modified	PF45 Psm	12.3 (1 bar)	100% ^e		70	
Original	PVDF				88	SSS/AA, electron beam [19]
Modified	PVDF-g-SSS/AA				62	
Original	PVDF	180.4 (1 bar)	0.27 μm ^f	30% ^g	102.3	PEGMA, electron beam [156]
Modified	PVDF-g-PEGMA	226.1 (1 bar)	0.47 μm ^f	85% ^g	51.0	
Original	PVDF 0.45 μm, Millipore		1.11 μm ^h			2-Vinylpyridine, ATRP [157]
Modified	PVDF-g-poly(2-vinylpyridine)		0.98 μm ^h			
Original	PVDF				84 or 58	MMA and PEGMA, ATRP [158]
Modified	PVDF-g-PMMA or PVDF-g-PPEGMA					
Original	PVDF	140–20			85	SBMA, ATRP [159]
Modified	PVDF-g-polySBMA	90–80	72%	89%, 100%	52	
Original	PVDF	95 (1 bar)		55.5%	80	PEGMA, thermal-induced, ATRP,
Modified	PVDF-g-PEGMA	80, 60, 4.5 (1 bar)		90.8%	60	Plasma [160]
Original	PVDF			0.18 ⁱ	93	PEGMA, DMAEMA, ATRP [161]
Modified	PVDF-g-PPEGMA or PVDF-g-PDMAEMA			0.02 ^j	78, 73	
Original	PVDF 0.45 μm, Millipore	1080 (0.09 MPa)	1.42 μm ⁱ	0.28 ^j	124	MMA, PEGMA, RATRP [162]
Modified	PVDF-g-PMMA, PVDF-g-PPEGMA	10,440 (0.09 MPa)	0.75 μm ⁱ	0.08 ^j	94, 87	
Original	PVDF				93	MMA, PEGMA, RAFT [163]
Modified	PVDF-g-PPEGMA or PVDF-g-PMMA				78, 73	

^a Pore size of the membrane calculated based on Poiseuille's equation.

^b The protein rejection of homogenized milk with 3.2% protein.

^c Pore size of the membrane determined based on Young–Laplace's equation.

^d Rejection of bovine serum albumin (BSA) with a molecular weight 68,000 g/mol.

^e Rejection of positively charged methylene blue.

^f Mean pore size of the membrane measured by a mercury porosimeter.

^g The relative flux ratio J/J_0 after 3 h filtration, J , flux of 1.0 g/L BSA, J_0 , flux of pure water.

^h Number-average pore diameters of the membranes.

ⁱ Mean pore size of the membrane surface determined by Micro-image analysis and Process software.

^j $[N]/[F]$ ratio expressing the relative amount of BSA adsorbed onto the membrane surface.

monomers in the absence and presence of the photo-initiator [150]. Both of these two types of membranes exhibited decreased pure water flux due to the reduction of the pore size. However, the milk water permeation and protein rejection of treated membranes were improved and the antifouling properties and flux recovery of the modified membrane were enhanced. The flux recovery after water washing could reach 62%. Instead of adding the photo-initiator, another way to modify the PVDF membrane using UV was to blend a small amount of photoactive poly(ether sulfone) (PES) in PVDF [151], and then the grafting polymerisation was initiated on the blend membrane through UV. The addition of PES in the PVDF membrane did not change the mechanical strength within the content of PES in 3.3 wt%; however, it made the photo grafting on PVDF possible. The modified membrane showed better fouling resistance than the original PVDF membrane, due to the increase of hydrophilicity. The adsorption amount of bovine serum albumin (BSA) on the membranes decreased from $159 \pm 2 \mu\text{g}/\text{cm}^2$ to $13 \pm 2 \mu\text{g}/\text{cm}^2$ after 10 min of grafting. The filtration of a 0.1% BSA solution showed that the modified membrane had a lower BSA adsorption and better flux recovery.

4.1.2.2. Plasma. Plasma is an efficient way to anchor the functional graft chains on the surface of PVDF membrane. Plasma treatment is usually limited to the membrane surface due to the lower energy of plasma and high stability of PVDF membrane, and hence the bulk properties of the membrane still remain unaffected. The thickness of the modified layer can be controlled up to the angstrom levels [152,167]. Hydrogen-, argon-, helium-, oxygen-, nitrogen- and fluorine-containing plasmas are frequently used to modify the membrane surface. The charged and neutral species produced by plasma in different gases include electron, positive ion, negative ion, radical, atom, and molecule. The ionized species abstract hydrogen atoms from PVDF and produce the initiating sites on the membrane surface to initiate the polymerisation of functional monomers. The main disadvantage of plasma is that it requires a vacuum system, which increases the cost of the operation [167].

The surface properties of electrospun nanofibrous membranes can be altered through plasma initiation via multi-steps [152]. The membranes were firstly exposed to argon plasma, and then exposed to air for a desired time to facilitate the formation of surface oxide and peroxides. Lastly, the surface active membrane was grafted by hydrophilic methacrylic acid [152]. The pore size of electrospun nanofibrous membranes grafted by methacrylic acid reduced from 3.6 to 0.9 μm and therefore it can be considered as a microfiltration membrane, similar in pore-size distribution with a commercial 0.45 μm hydrophilic phase inversion membrane (HVHP, Millipore, USA) but with a significantly better flux. So plasma induced grafting indicated another way to develop micro- or ultra-filtration membrane from electrospun nanofiber membranes.

Besides methacrylic acid, another common hydrophilic grafted monomer is poly(ethylene glycol) (PEG) [153]. A layer of PEG was firstly coated on the surface of the membrane, including the surface of the pores by dipping the membrane in a chloroform solution of PEG. The membrane was then exposed to argon plasma to initiate the grafting polymerisation. It was found that the water flux decreased with the increase of grafting degree, while the mean pore size remained almost unchanged. The protein adsorption experiment revealed that the PVDF-PEG membrane with a graft concentration ($[\text{CO}]/[\text{CF}_2]$ ratio) above 3.2 exhibited good anti-fouling property. With the exception of hydrophilic monomers, hydrophobic monomers like styrene could be grafted to membrane to decrease the pore size and narrow the pore size distribution, which resulted in the higher contact angle, reduced water flux and increased BSA rejection. It was suggested that the grafting sites were produced by the cleavage of weaker C–H bonding (413 kJ/mol)

by argon plasma, which produced a great number of free radicals and initiated the subsequent grafting polymerisation [154].

It was reported that low temperature plasma treatment can be directly used to modify the PVDF membrane surface with the reactive gas ammonia-fed discharge. The modified membrane with a rich surface of N-containing functionalities (NH, NH₂, OH, etc.) increased the surface tension and enhanced the hydrophilicity [155]. Due to the positively charged properties originated from the N-containing moieties, the modified membrane (PF45psm) exhibited 100% retention and a relative flux of 65% for methylene blue (positively charged) as a nanofiltration membrane. All other properties of the modified membrane are listed in Table 8.

4.1.2.3. Electron beam. Comparing the less active initiating ability of UV and plasma to PVDF membrane, high energy irradiation (e.g. electron beam and gamma ray) is another efficient way to activate PVDF membrane and initiate the grafting copolymerisation of functional monomer on the membrane surface. The G value for radical formation of PVDF on γ -radiolysis under vacuum at ambient temperature is 3.3 (The G value is the number of species formed or the number of chemical changed of a particular type induced on the deposition of 16aJ (100 eV) of energy) [20]. The radicals induced by electron beam are believed to be principally located in the crystalline-amorphous interphase regions in PVDF. The stable radicals are predominantly chain-end and main-chain radicals arisen from the cleavage of main chain carbon–carbon bonds and carbon–fluorine bonds. The long-live radicals formed in the PVDF chain made the pre-irradiation grafting method possible, which produced less homopolymerisation than simultaneous grafting method and peroxy method, since monomers are not directly exposed to irradiation [20].

A great motivation to accelerate much of the current research into grafting fluoropolymers is the prospect of being able to produce an alternative to the very costly fuel cell membrane Nafion [168,169]. However in this study, hydrophilic modification of the PVDF membranes is performed to treat drinking water or wastewater. Binary monomers of acrylic acid (AA) and sodium 4-styrenesulfonate (SSS) can be introduced to the PVDF membrane surface by a single step method. The binary monomer ratio and pH of reaction solution affect the degree of grafting. It was found that AA diffused onto active sites of the PVDF membrane due to better compatibility, and then sphere hydrated SSS could diffuse onto the PVDF membrane with improved hydrophilicity. The contact angle of membrane modified under optimum monomer ratio and pH value decreased from 62° to 0° in only 25 s [19].

A disadvantage of these linear grafting chains is that the graft chains grow long at high degree of grafting, and the long straight chains may consequently minimize or even plug the pores. Therefore, the grafted chains with special topologies, e.g. comb-like brushes would be preferred. The PVDF membrane was first pre-irradiated with the high energy electron beam, and then the activated membrane reacts with the hydrophilic monomer of poly(ethylene glycol) methyl ether methacrylate in an aqueous solution [156]. Pure water flux of the modified membrane increased from 180 to 226 L/m² h because of the enhanced hydrophilicity and pore size. The electron beam irradiation induced the chain scissions especially in the crystalline-amorphous interphase regions and caused an increase in the molecular chains mobility [170]. The increasing movement of PVDF chains resulted in the chain crosslinking in the amorphous region. The appropriate scission and crosslinking contributed to the slight increase of pore size. Both ¹H NMR and XPS results confirmed that the hydrophilic side chains (PEG) of grafted PEGMA stretch out of the membrane surface due to the special comb-like architectures without blocking the internal pores of the membrane. All other properties of the modified membrane are listed in Table 8.