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Hydrophilic Modification of PVDF Membrane: a Review

Herlambang Abriyanto[1,2*]

[1]*Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, INDONESIA 50275*
[2]*Membrane Research Center (Mer-C), Diponegoro University, INDONESIA 50275*

**Corresponding author :* herlambang.abri@gmail.com

Abstract. The key challenges faced by using membranes in carrying out this water treatment process are increasing filtering efficiency and reducing the cost of water treatment. PVDF is one of the most widely used membrane materials, and its outstanding properties, such as high mechanical strength, thermal stability, chemical resistance and hydrophobicity, have received a great deal of attention from researchers and manufacturers in recent years. However, the strong hydrophobic properties of pure PVDF membranes, when handling aqueous solutions containing some natural organic and colloidal materials which are susceptible to deposition and absorption to the membrane surface, often lead to low water permeability and fast fouling. There are many methods of modification to change the properties of the antifouling membrane surface by physical modification (coating, mixing and use of composite membranes) and chemical modification (polymer functionalization, plasma processing and graft polymerization). Several methods of increasing the hydrophilicity value of membranes, such as surface coating, surface grafting and plasma polymerization, will be presented in this review paper.

Keywords: fouling, hydrophilicity, membrane, modification, PVDF

1. Introduction

It is not possible to ignore the rising number of people on earth, which has an effect on the state and balance of the current ecosystem. One of them is the state of water that is increasingly contaminated and unsanitary to use in the world. Humans are now competing to build technologies for water treatment so that it can be reused. This technology can be an alternative option to replace other separation technologies or even be used with other separation technologies in an integrated way, since there are many important advantages of using membranes for industrial processes, such as no phase change or chemical addition, easy to update modular, easy to operate, relatively low energy consumption, etc.

In various fields such as water treatment, gas purification (Zhang et al., 2013), food processing (Charcosset, 2009), the pharmaceutical industry (Zaviska et al., 2013) and environmental conservation, membrane technology has therefore been widely used.However, of the many uses of this membrane technology, water treatment and wastewater treatment are the ones that most utilize membrane technology in overcoming these problems.In carrying out this method of water treatment, increasing filtering efficiency and reducing water treatment costs are the key challenges facing the use of membranes.

The sieving method with a moving force in the form of pressure is the method used in the process of filtering water with a membrane. Pressure-activating membrane processes are categorized into membrane microfiltration (MF), UF, nanofiltration (NF), reverse osmosis (RO) and are based on variations in membrane pore size. Fouling is the key issue that is often faced in the filtering process, apart from the difficulty of increasing the filtration performance of membranes. Fouling is the blockage by dirt or contaminants of membrane pores present in the feed solution to be filtered. Membrane impurities are recognized as a key element as they both temporarily and permanently reduce membrane flux. Membrane impurities are considered a major problem as they both temporarily and permanently reduce membrane flux. Therefore, in addition to mechanical, thermal and chemical properties, many membrane researchers worldwide are competing to conduct research to enhance the efficiency of membranes that have strong anti-fouling properties. Properties of membranes. Better still. The engineering process in improving membrane performance can be carried out in various ways, including modifying the operating conditions of the membrane to reduce fouling and increase the flux value. Using a good membrane material, modifying the constituent material of the membrane, adding compounds that have good antifouling properties.

At present, almost all membranes used in industrial processes are made of inorganic materials and / or organic polymers. Examples of organic polymers include PVDF, polysulfone (PSF), poly (ether sulfone) (PES), polyacrylonitrile (PAN), polyamide (PA), polyimide (PI) and polytetrafluoroethylene (PTFE). Of these, PVDF is one of the most commonly used membrane materials and, in recent years, has received a great deal of attention from researchers and manufacturers with respect to its outstanding properties, such as high mechanical strength, thermal stability, chemical resistance and hydrophobicity. (Liu et al., 2011). However, the strong hydrophobic nature of pure PVDF membranes always causes low water permeability and is easily contaminated when processing aqueous solutions containing several natural organic and colloid materials, which are susceptible to deposition and absorption into the membrane surface (Brites Alves et al., 2002). Therefore, much of the research on PVDF membranes has focused on increasing hydrophilicity through various methods, including improving membrane separation processes and modification of existing membrane surfaces (Cao, 2014).

2. Membrane PVDF

The membrane of polyvinylidene fluoride (PVDF) is a pure thermoplastic fluorine polymer formed by vinylidene difluoride polymerization with the chemical formula C2H2F2. Due to its excellent anti-oxidation activity, PVDF is one of the most widely used membrane materials in recent times for oil separation from oily wastewater, Highly organic selectivity, strong mechanical forming strength that enables re-examination and storage, excellent processing facilities (Masuelli, 2013), ease of control of structural and morphological characteristics, excellent aging resistance, high binding power, excellent chemical resistance and thermal stability, large processing temperature and ductility shown in Table 1. In contrast to other organic polymers such as PSF, PES, PVDF is relatively more hydrophobic, which may not be as high as polypropylene (PP) and polytetra fluoroethylene (PTFE). Generally, the hydrophobicity of polymeric materials is generally associated with their critical surface tension. PVDF is readily soluble in common organic solvents such as N, N-dimethylacetamide (DMAc), N, N-dimethylformamide (DMF), N-methylpyrrolydone (NMP) and Acetone, and as a result, the porous PVDF membrane is readily formed via non-induced phase separation. solvent (NIPS). Apart from that, its excellent thermal stability, semi-crystalline properties have made PVDF an attractive membrane material. The ability to choose the right material for the formation of PVDF membranes as well as the best membrane preparation techniques play a very important role in the performance of PVDF membranes.

Such factors, however, may not be sufficient to achieve top results. Phase inversion, interface polymerization, electro spinning, stretching, and traverse etching are the most widely used techniques for the preparation of PVDF membranes. The most widely used techniques for the manufacture of PVDF membranes are phase inversion, interface polymerization and electro-spinning, among the previously described techniques. A controlled transformation of a thermodynamically stable or homogeneous polymer solution from a liquid to a porous solid is involved in the phase inversion process. Non-solvent-induced phase separation (NIPS), thermally induced phase separation (TIPS), evaporation-induced phase separation (EIPS), and phase separation steam-induced (VIPS) can induce phase separation from the casting solution to the lean PVDF polymer and the rich phase of the PVDF polymer (Lalia et al., 2013).

Table 1. Characteristics of PVDF (Lovinger, 1981)

Character	**Value**
Form	White solid
Solubility	Non-soluble in water
Elongation	12 – 600%
tensile strength	21,0 – 57,0 MPa
modulus of elasticity	1380 – 55.200 MPa
Glass temperature transition (Tg)	-60 – -20^{o}C
Melting Temperature	141 – 178^{o}C

Although, these reasons may not be sufficient to achieve top performance. The most commonly used techniques for the preparation of PVDF membranes include phase inversion, interface polymerization, electro spinning, stretching, and traverse etching. Among the previously mentioned techniques, phase inversion, interface polymerization and electro-spinning are the most commonly used techniques for the manufacture of PVDF membranes. The phase inversion process involves a controlled transformation of a thermodynamically stable or homogeneous polymer solution from a liquid to a porous solid. The phase separation from the casting solution to the lean PVDF polymer and the rich phase of the PVDF polymer can be induced by: non-solvent-induced phase separation (NIPS), thermally induced phase separation (TIPS), evaporation-induced phase separation (EIPS) and phase separation steam-induced (VIPS) (Lalia et al., 2013).

3. Hydrophilic membrane and antifouling

The hydrophilic-hydrophobic design of the polymer material that makes up the membrane is one of the essential aspects in the process of membrane filtration. By looking at the angle of touch between the membrane surface and the liquid, this property can be determined. A broad contact angle of 90 ° or more is characterized by hydrophobic properties, whereas numbers below

90 ° are known as hydrophilic materials (Yuan, 2013). Polymeric materials are typically membranes with hydrophobic constituents such as PES, PSF, PAN and PVDF for processes that use pressure as a forced drive. This is because this polymer has very good mechanical, chemical and thermal properties, but due to strong adhesion-adsorption forces, it is very susceptible to fouling due to foulant interactions with the membrane surface, almost no hydrogen bonding interactions in the boundary layer between the membrane interface and water (Kochkodan & Hilal, 2015). The repulsion of water molecules moving away from the hydrophobic membrane surface is a random phenomenon that causes foulant molecules to begin to adsorb to the surface of the membrane and to control the boundary layer and the process of polarization of concentration that occurs during the process of filtration.

In comparison, high surface tension membranes with hydrophilic layers are capable of forming hydrogen bonds with adjacent water molecules for the reconstruction of the thin water boundary between the membrane and the condensed liquid. This layer will avoid or minimize contaminants attached to the surface of the membrane (Kochkodan & Hilal, 2015). In this case, the fouling-resistant membrane not only decreases protein adsorption greatly, but is also capable of preventing microbial adhesion.

4. PVDF membrane surface modification

There are many methods of modification to transform the properties of the membrane surface into antifouling by means of physical modification (coating, mixing and use of composite membranes) and chemical modification, according to (Ayyavoo et al., 2016) (polymer functionalization, plasma processing). And polymerization of the graft).

Three different mechanisms physically place hydrophilic functional materials on the membrane surface: (1) macroscopic binding of functional groups and membrane pore structures, (2) interpenetration through the interface combination of functional materials and simple polymers, and (3) adhesion/adsorption (Ayyavoo et al., 2016).

4.1.Surface coating

In the case of a surface coating, the membrane is soaked in a polymer-containing solution in order to enhance the properties of the current antifouling membrane (Lalia et al., 2013). Poly (vinyl alcohol) (PVA), chitosan and poly (block ether amide) (PEBAX) are hydrophilic polymers which are commonly used due to the poor physical adsorption interaction between PVDF membranes and layered layers for hydrophilic modification of PVDF membranes (Kang and Cao, 2014). During the operation, the latter appears to be lost. Surface grafting, on the other hand, may be applied to the membrane surface to overcome the instability issue of the coated layer. The surface modification path, including surface resurfacing and surface grafting, is shown in Figure 1. (Liu et al., 2011). Due to its high hydrophilicity, biocompatibility, mechanical strength and thermal stability, PVA can be used as a hydrophilic surface for membranes

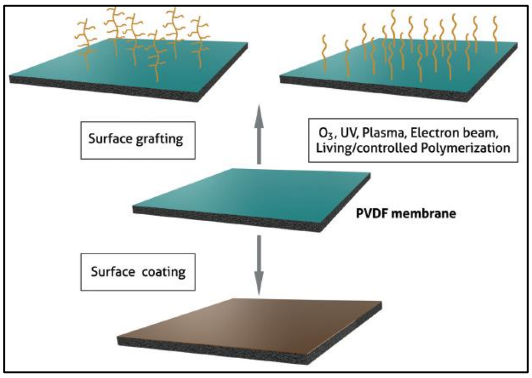

Figure 1. The route of surface modification, including surface coating and surface grafting (Abed K.Li, 2011).

In addition, improved biofouling resistance has been shown by PVA coated surfaces. The contact angle decreased from 81 ± 1 ° to 68 ± 1 ° after modification, with the addition of PVA (Du et al., 2009). The modified membrane displayed a greater flux and slower fouling rate relative to the unmodified membrane during natural water filtration. A double-layered PVDF hollow fiber membrane (HFM) was modified by coating it with dopamine and grafting polyethylene in a study conducted by Shi et al (2016). Through the quaternization reaction shown in Figure 2, researchers obtained hydrophilic and antibacterial membranes. The results obtained were the pure water flux value (PWF) before and after the bovine serum albumin contamination (BSA) measurement, and the rate of flux recovery. The changed membrane had reached 94.%.

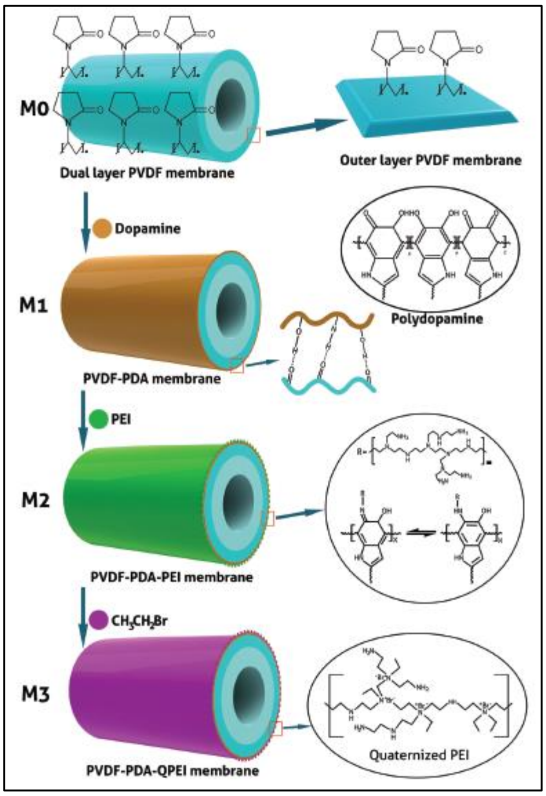

Figure 2. A hydrophilic and antibacterial membrane through quaternisation reactions (Shi et al,2016).

4.2.Surface grafting

Transplants are carried out by changing the membrane surface surface by covalent bonding interactions between hydrophilic compounds and membranes in the chemical chain. The covalent bond on the surface of the resulting membrane, unlike the surface layer, would have greater chemical stability than that of the surface layer. The technique of surface grafting, however, has a weakness, namely that the graft compound can block the membrane pores and reduce the performance of the membrane, namely the permeability and flux produced (Moghareh Abed et al., 2013). In several models, such as plasma treatment grafting, managed polymerization grafting and UV photography, the surface grafting process can be carried out. Rahimpoor with a scientific dip coating was an example of changing the PVDF membrane, followed by UV irradiation using benzophenone as a photoinitiator. In order to improve hydrophilicity, they used acrylic acid (AA) and 2-hydroxyethylmethacrylate (HEMA) as acrylic monomers and 2,4-phenylenediamine (PDA) and ethylene diamine (EDA) as amino monomers at different concentrations, thereby minimizing fouling tendencies. After alteration, the PVDF membrane's hydrophilicity, antifouling properties and flux recovery were all enhanced.

4.3. Plasma polymerization

The electrical ionization of the monomers is plasma polymerization, resulting in fragments of reactive monomers. The benefits of plasma polymers over traditional polymers are that this technique has a much higher degree of cross-linking and is tightly bound to the substrate, and the coating is uniform and does not require the use of harsh solvents that can damage the substrate (Zou et al., 2011).With rising surface PEG graft concentrations, the researchers found that PWF decreased, while the mean pore size remained almost unchanged. In addition, the experiments on protein adsorption and water flux showed that the PEG-g-PVDF membrane exhibited strong anti-fouling properties with a graft concentration ([CO] / [CF2]) above 3.2 as a simple dipping coating technique using inverted super-hydrophilic silica nanoparticles on a poly (methacrylic acid) copolymerized membrane surface (PMAA) (Liang et al., 2013) shown in Figure 3.

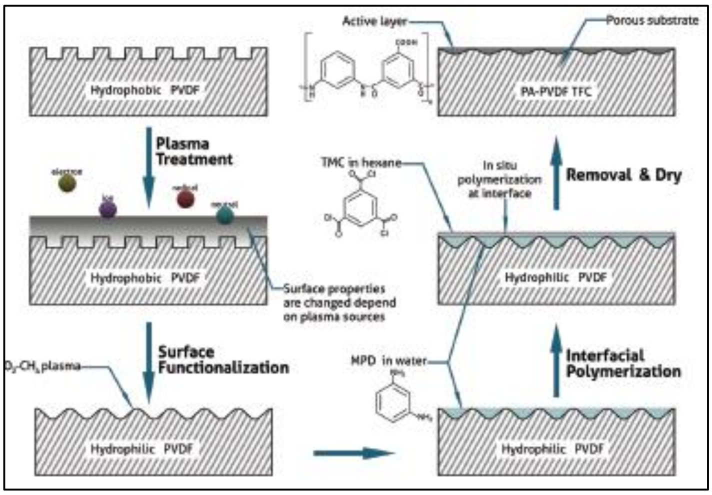

Figure 3. Using the post-fabrication method, super-hydrophilic silica nanoparticles are irreversibly bound to the poly(methacrylic acid) (PMAA) graft-copolymerised PVDF membrane surface using a simple dip-coating technique (Liang et al, 2013).

With this process, modification is capable of changing the properties of the PVDF membrane from hydrophobic to hydrophilic conditions and forming a layer of hydration on the -OH group. It also has excellent antifouling properties (Liang et al., 2013).

5. Conclusions

In the treatment of aqueous solutions containing some natural organic and colloid materials, which are susceptible to deposition and absorption to the membrane surface, the strong hydrophobic properties of pure PVDF membranes often lead to low water permeability and fast contamination. There are many methods of modification to alter the surface properties of the antifouling membrane by physical modification (coating, mixing and use of composite membranes) and chemical modification (polymer functionalization, plasma processing and graft polymerization). Several methods of increasing membrane hydrophilicity, such as surface coating, surface grafting, and plasma polymerization, will be addressed in this review article.

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