A Direct Comparison Between Poly(vinylidene) Flouride and Polysulfone Flat Sheet Membrane; Characterization and Mechanical Strength

A. Febriasari¹, I. Purnawan¹, M. Chalid², I. Ismojo², S. Kartohardjono*¹
¹ Department of Chemical Engineering, Universitas Indonesia, Kampus UI, Depok 16424, Indonesia
² Department of Metallurgical and Material Engineering, Universitas Indonesia, Kampus UI, Depok 16424, Indonesia

*Corresponding email : sutrasno@che.ui.ac.id

Abstract. Selecting a proper material is the first key step for determining suitable membrane application. Hence, the comparison of membrane properties is urgently required to be conducted. This work aimed to compare two common materials of polymer flat sheet membranes, i.e poly(vinylidene) fluoride (PVDF) and polysulfone (PSf), from preparation to characterization. Phase inversion method was applied for both materials using different solvent. PVDF was dissolved in N, N-dimethyl acetamide (DMAc) whereas PSf was dissolved in N-methyl pyrrolidone (NMP) with the same composition ratio of polymer and solvent. The properties of membranes were investigated by FTIR, FE-SEM, water contact angle, and Universal pull machine. FE-SEM result indicates that PSf membrane has larger pores than PVDF membrane. Meanwhile, water contact angle analysis describes that PVDF membrane is more hydrophilic than PSf membrane.

Keywords: membranes, polymer, poly(vinylidene) flouride, polysulfone

1. Introduction

Membrane technology is widely used for separation, such as; wastewater treatment, gas separation, haemodialysis, distillation, oil/water separation, etc. Membrane technology has advantages compared to other separation methods, i.e.; require small place, simple and efficient process, produce high quality effluent with low solid waste, and no chemical needed [1-3].

Various types of membrane material have been used in several separation processes. Polymer membranes are currently the most widely used for several types of membrane applications, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [4-6]. Polymeric materials that are often used for membrane applications include; cellulose acetate (CA), polypropylene (PP), Polysulfone (PSf), poly(vinylidene) fluoride (PVDF), etc [7-10]. Each of these polymers has different characteristics so that the selection of the right polymer material for a particular...
application is needed. In this study, a comparison in mechanical properties, morphology, and hydrophilicity between polymer membranes made from PVDF and PSf was conducted.

Since it has excellent properties as a polymer membrane with the good chemical, thermal, and mechanical stability, polysulfone (PSf) is commonly used for ultrafiltration in various pH operation range [11]. However, the ease of fouling becomes the main weakness of polysulfone which is caused due to its hydrophobic nature [12, 13]. PVDF is also one of the polymers that are widely used as membrane materials. Some references said that PVDF has good thermal and mechanical stability. This membrane is also resistant to reactive chemical attack. In addition, PVDF membrane hydrophilicity and porosity can be regulated by variations of casting techniques and additives.

In this case the characteristics of the PSf membrane will be compared with the PVDF membrane by observing the membrane surface morphology, hydrophilicity, and mechanical stability of the membrane. Comparison tests between the two polymer materials will be able to assist researchers in determining the use of the right membrane for applications according to the character of the two polymers.

2. Materials and methods

2.1. Materials

This work used materials such as PSf (1700NT) and 6012 PVDF were purchased from Solvay Chemical. N, N dimethyl acetamide (DMAc) and N-methyl pyrrolidone (NMP) as a solvent for membranes were purchased from Merck. Deionized water and ethanol 96% were purchased from PT. Dwinika Intan Mandiri.

2.2 Polysulfone Membrane preparation

The PSf membrane was made by dissolved it in NMP solvent with a PSf and NMP ratio of 15:85. The dissolution method was carried out as follows; NMP solvent was placed in the Erlenmeyer flask and then slowly added PSf at 25 °C with 200 rpm stirring. Mixing process is continued by raising the temperature to 60 °C and stirring speed of 300 rpm until the polymer was dissolved. Then the stirring continues until a homogeneous solution is formed for 3 hours with a stirring speed of 500 rpm. Homogeneous PSf solution is then allowed to stand in the room temperature until the foam formed disappears.

The PSf solution is then poured into a glass plate, then flattened with a glass rod so that the thickness is evenly distributed. The glass plate is then put into a container filled with deionized water until it is submerged. The formed membrane is then immersed in deionized water for one night, then washed by immersing it in 96% ethanol for 1 hour. The membrane is then allowed to stand at room temperature until it dries and is ready to be characterized.

2.3 PVDF membrane preparation

The PVDF membrane was made with DMAc solvent in the same ratio as PSf, which is 15:85. The DMAc solvent which had been placed in the Erlenmeyer container was then slowly poured PVDF into it for 30 minutes at 25 °C at a stirring speed of 200 rpm. Then the temperature is raised to 60 °C with a stirring speed of 500 rpm until PVDF completely dissolves for up to 4 hours. After homogeny, the solution is then allowed to stand until the foam disappears. The PVDF solution is then casted using the same method as the PSf membrane above.
2.4 Membrane morphology characterization

The membrane that has been formed is then characterized by FTIR, FE-SEM, and water contact angle. FTIR analysis was performed using Thermo Scientific FTIR (Diamond Nicolet IS 5). The spectra were recorded at 32 cm\(^{-1}\) resolution by 64 scans between 500-4000 cm\(^{-1}\). Scanning electron microscopy (SEM) (FEI Inspect F50) was employed to observe the surface morphology of membranes. The specimens were coated by a thin layer of Au and the morphology thin layer was observed at 20.0 kV of excitation voltage.

Water contact angle analysis was carried out to determine the hydrophobicity of the membrane surface. In this study, a set of contact angle measuring devices was used with measurements made three times randomly. Deionized water is used as a liquid probe for each measurement.

2.5 Mechanical strength measurement

Membrane mechanical tests were carried out by measuring tensile strength and percentage of elongation using Universal Pull Machine with dimensions of length and width of polymer membranes of 40 x 25 mm each. Membrane’s tensile strength is calculated by the formula:

\[
\sigma = \frac{F}{A_0}
\]

Where \(\sigma\) is tensile strength of membrane (MPa), \(F\) is the load during the measurement, and \(A_0\) is surface area of membrane. Meanwhile, the strain or percentage of elongation was measured by the equation below:

\[
\varepsilon = \left(\frac{\Delta L}{L_0}\right) \times 100
\]

The symbol \(\varepsilon\) describe the percentage of elongation, \(\Delta L\) is the corrected extension of the membrane during the test, and \(L_0\) is the length of membrane [14].

3. Results and discussions

3.1. Membrane casting process

In the phase inversion technique, membrane deposition is formed because of the large solubility difference between polymer and non-solvent as a precipitant. When the polymer solution is immersed in a non-solvent, the dispersion of the polymer to the organic solvent is reduced to be replaced by the non-solvent. In this study, PVDF solution takes longer to precipitate in water compared to PSf. The solubility factor of the polymer with the solvent used also affects the duration of the deposition process in the polymer. The smaller solubility disparity of the polymer and the solvent, the longer it takes for the dispersion change between the polymer, solvent and non-solvent [15-17]. This also affects the formation of membrane pores as confirmed by the results of the FE-SEM characterization (point 3.3).

3.2 The mechanical properties

The stress-strain curves in Figure 1 show the comparison of mechanical behavior of PVDF and PSf membrane from experimental results. The yield strength point in the curves (0.77 MPa for PSf and
0.21 MPa for PVDF) describe that elastic deformation area of PSf is wider than the elastic deformation area of PVDF. The higher elongation at break of PVDF membrane describes the ductility of the membrane. These results also indicate that PVDF is easier to swelling. Meanwhile, the higher transverse direction of strain hardening area shows that PSf is a stiffer polymer material with higher tensile strength [18]

![Graph showing stress-strain curves comparison between PSf and PVDF membranes](image)

Figure 1. Stress-strain curves comparison between PSf and PVDF membranes

| Membrane | Ultimate tensile strength (MPa) | Yield strength (MPa) | Elongation at break (%) |
|-----------|-------------------------------|---------------------|-------------------------|
| PSf       | 0.88 ± 0.0047                 | 0.77 ± 0.0091       | 28 ± 1.08               |
| PVDF      | 0.32 ± 0.0017                 | 0.21 ± 0.0065       | 171 ± 0.05              |

The characteristics of the polymer membrane can affect the mechanical behavior of the membrane material, both the morphological character and chemical structure of the polymer membrane. Anisotropic membranes have more rigid mechanical properties with higher tensile strength values [17]. This statement is supported by the compatibility between the results of mechanical tests with FE-SEM membrane PSf tests. Where this membrane has an uneven pore size and tends to be larger compared to PVDF (Figure 2 and 3).

The molecular structure of the polymer also affects the mechanical properties of membranes. Sgreccia et al. (2010) state that large plastic domain is usually owned by polymers that have linear chains. This is related to the weakness of Van der Waals bonds so that polymer solutions with straight
bonds tend to be more viscous and form more flexible polymer membranes. Conversely, the presence of covalent bonds in the aromatic polymer compound will make the membrane more rigid so that the plastic deformation area is shorter [19, 20]. This statement is confirmed by the results of the analysis of the polymer functional groups in Figure 4.

3.3 Membrane morphology

Differences in the characteristics of PVDF and PSf membranes were compared by conducting several analyzes, including FTIR, SEM, and water contact angle. The results of the FE-SEM characterization were carried out in Figures 2 and 3. Figure 2 confirmed that the pore size of the PVDF membrane is smaller (0.34 µm) compared to PSf (1.39 - 2 µm).

![Figure 2. FE-SEM results of PVDF and PSf membrane with 5000 times of magnification](image)

![Figure 3. FE-SEM of PVDF and PSf membrane cross section with 500 times of magnification](image)

PVDF in organic solvents has a low critical surface tension (about 25 nM/m) so that it causes the longer process of membrane formation during phase inversion which also impacts on the slow formation of membrane pores [17]. The slow process of membrane formation by coagulation in water is also due to the functional groups possessed by PVDF, where the C-F bond in PVDF causes PVDF to be more hydrophilic compared to PSf. This hydrophilic nature cause greater PVDF solubility to
water compared to PSf, so PVDF is more difficult to coagulate. This difference in functional groups is confirmed by the results of the analysis in the FTIR test. Some researchers add certain additives, such as polyvinylpyrrolidone (PVP) and poly(ethylene glycol) (PEG) to be able to regulate and increase the porosity of the PVDF membrane [21, 22]. Meanwhile, PSf with higher surface tension (about 41 mN/m) and aromatic groups on the chemical structure makes it easier to precipitate in the water so that membrane pores are more easily formed [23-25]. This is also evident in the cross section of the membrane FE-SEM result in Figure 3 where the pores formed on the PSf membrane appear more tenuous and larger than PVDF. The difference in porosity shown by the SEM results also proves compliance with the membrane mechanical properties test, where larger pores cause the membrane to tend to be stiffer compared to smaller pore sizes.

This porosity difference can also make it easier for researchers to determine the appropriate application for the use of the membrane material. PVDF with smaller pore size will certainly be more selective towards molecules with smaller particle diameters.

3.4 FTIR Study

The results of the FTIR analysis are shown in Figure 4 where the PVDF spectra show the peak at wavenumber of 1174.5 cm$^{-1}$ identifying the stretching vibrations at CF$_2$. Peak at 1401.32 cm$^{-1}$ showing the stretching and deformation of the CH$_2$ alkane bond [26, 27]. In addition, weak peaks at 2920.63 and 2442.11 cm$^{-1}$ also indicate CH stretching in PVDF and DMAc aldehyde groups [28].

![Figure 4. FTIR spectra of PSf (top curve) and PVDF (bottom curve) membranes](image)

PSf spectra show the peak at 2966.54 cm$^{-1}$ which is the vibration of CH bonds in aromatic compounds. Peaks at 1486.42 and 1583.63 cm$^{-1}$ describe the presence of vibrations of C = C aromatic compounds on polysulfone [27]. The results of this analysis are in accordance with the molecular structure of PSf and PVDF as illustrated in Figure 5.
Based on the results of mechanical, morphology, and contact angles tests, the molecular structure of these two membrane polymers has an important role in determining the mechanical properties, porosity, and hydrophilicity of a flat sheet membrane. PSf with aromatic compounds have higher tensile strength values with stiffer material properties compared to aliphatic PVDF. The hydrophilicity of PVDF is caused by the presence of C-F bonds which are more likely to bind water, which in fact can also affect the formation of pores of the membrane.

3.5 Water contact angle

The next characterization comparison is the analysis of water contact angle on the membrane surface. The results of the water contact angle analysis are shown in Figure 6, where the PVDF membrane has a smaller contact angle value compared to the PSf membrane. Li et al. (2009) proved that the exposure time of the membrane solution in the glass plate before the membrane coagulation process can affect the hydrophobicity of the membrane. The longer the time of exposure before the coagulation process, it will provide an opportunity for the solvent to evaporate first, this can accelerate the deposition of the membrane when coagulated in a coagulation bath and enlarge the membrane pores. According to that research, the larger the membrane pores, the more hydrophobic the membrane surface is [29].

In this study, the casting process on the both membranes was not carried out exposure to the polymer solution on the glass plate before coagulation. After casting with the glass rod, the polymer solution on the glass plate is immediately dipped in a coagulation bath, so the pore formation process majority occurs during the coagulation process in the coagulation bath. It is majority depend on specific behavior of the polymer to form the pores. The specific behaviors of membranes are related to the molecular structure and the porosity of membranes. Water contact angle analysis show that PVDF is more hydrophilic compared to PSf.
Conclusions

PVDF and PSf membranes can be formed by the same method, i.e. phase inversion method. The precipitation process in the coagulation bath, showed that the PVDF membrane takes a long time to precipitate and form a pore compared to the PSf membrane. According to the mechanical properties analysis, PSf membrane has a higher tensile and yield strength with a more stiff nature than PVDF membrane. The mechanical properties and hydrophilicity of membranes were affected by the morphology and molecular structures. The FE-SEM and contact angle analysis results show that the PSf membrane forms larger pores with more hydrophobic properties compared to PVDF.

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