Comparison of Physical and Mechanical Properties of Antifouling PVDF Membranes by Titanium Dioxide and PES Membrane by Titanium Dioxide

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Abstract. The main factor to support daily life is water, but the fact is there are approximately 2.1 billion people currently threatened with a shortage of clean water. Polyethersulfone (PES) and Polyvinylidene Fluoride (PVDF) are polymers that are commonly used for membrane fabrication because they have extraordinary properties in the screening process. The addition of additive substances into the membrane formation process is no less important as supporting the ability to be even better in membranes Titanium Dioxide (TiO₂) as an additive with properties relevant to the two polymers which can cover the shortcomings of the two polymers. The printing process of PVDF and PES membranes with the addition of TiO₂ uses a copper plate which is flowed with an electric field of 15000V DC. The results of the surface morphology of Scanning Electron Microscopy (SEM) both showed extraordinary changes compared without modification to the printing process as in previous studies. The tensile strength test results showed uniformity with the membrane morphology and an increase in the maximum stress value of the membrane to 3.86 MPa. Surface roughness values can help identify membrane impurity properties which are also relevant to the results of water treatment performance tests and contact angles. Finally, the process of forming membranes with the additional modification of the printing process can open new avenues to maximize water treatment performance and service life on the membrane.

1. Introduction

In the past ten years, researchers have been intensively researching membrane fabrication. The research is a form of addressing water shortages as part of humans' primary needs. Polymer polyether sulfone (PES) and polyvinylidene fluoride (PVDF) are materials commonly used. As has been done by previous studies [1,2], PVDF and PES are membrane-making materials that have extraordinary filtration capabilities and are very beneficial in terms of function and cost.

However, behind the advantages possessed by the two polymer materials, PES and PVDF have the same disadvantages, namely their impurity properties. These impurity properties affect the filtration process up to the life of the membrane. The use of additive substances to the polymer will also make the fabrication of better polymers. Among those often used as additive substances is titanium dioxide (TiO₂). The titanium dioxide (TiO₂) role as an enhancer of impurity resistance that has been confirmed by [7] becomes an auxiliary electric field to overcome impurities in the polymer. Not only acts as an enhancer of impurity resistance, but titanium dioxide (TiO₂) also acts as an increase in hydrophilicity.
antibacterial, and self-cleaning of membranes [8]. In the study [9], [10], mixing titanium dioxide as an intermediary increased the hydrophilicity of the membrane. Also, the nature of titanium dioxide (TiO$_2$) has high electrical conductivity and the presence of hydroxy groups on the surface so that it has a high electrostatic interaction will play a role with a combination of modification of the addition of electric field currents in the membrane molding process [11], [12]. Despite the many advantages of titanium dioxide (TiO$_2$), it also has its drawbacks, [13] confirmed that mixing titanium dioxide (TiO$_2$) with a weight of 1wt% creates a lump called agglomeration and is one of the factors that can make the membrane worse. So in this study, the ratio of titanium dioxide (TiO$_2$) is locked with a composition of 1wt%.

2. Material and methods

PES and PVDF polymers, N, N-Dimethylformamide (DMF) solvents, and titanium dioxide (TiO$_2$) addictive substances obtained from Aldrich chemical (Indonesia) with no further purification processes. The compositions used are PES (Pure 25wt%, Mixed 20wt% & 30wt%), PVDF (Mixed 10wt%, 15wt%, 20wt%), TiO$_2$ 1wt%. Membrane formation begins with the process of mixing the PVDF polymers into the DMF solvent with Titanium dioxide and PES polymers into the DMF solvent with Titanium dioxide. Dissolution of membrane-making materials ranging from polymer, additives, and DMF using a magnetic stirrer with stirring for 8 hours. Modification of the membrane with the ready solution will continue with the flat sheet printing process. The membrane was modified using a copper plate energized by an electric field of 15000 V dc.

3. Results and discussion

In the current work, the test result shown the mechanical and physical properties of the PVDF with titanium dioxide membrane and PES with titanium dioxide membrane each specimen using a membrane tensile testing and for the physical properties using a scanning electron microscope to see the morphology of the membrane. Morphology for PVDF with titanium dioxide and PES with titanium dioxide shown in figure 1 and figure 2.

Based on figure 1 and figure 2 (a) provides information on the concentration of PES@TiO$_2$ 20wt% inhibited pore fabrication, this can be due to agglomeration of the membrane. Whereas the Pure PES 25wt% and PES@TiO$_2$ 30wt% significantly showed clearer pore formation. Figure 3.1 (b) the fine and tight pore size is observed. However, there are significant differences in the PVDF@TiO$_2$ membrane concentration of 10wt%, pore bonds have a large size compared to other concentrations so that it will affect the mechanical strength of the membrane. The pore size can be further caused by the addition of a 15000V DC electric field to help in pore leveling to prevent clumping of the membrane.

![Figure 1. SEM Polymer Observation PES with 3000 times Magnification (a) Pure PES 25wt% (b) PES@TiO$_2$ 20wt% (c) PES@TiO$_2$ 30wt%.](image-url)
Figure 2. SEM Polymers PVDF Observation with 1500 times Magnification (a) PVDF@TiO$_2$ 10wt% (b) PVDF@TiO$_2$ 15wt% (c) PVDF@TiO$_2$ 20wt%.

For the tensile strength of the membranes are using adhesion tearing stress to see the tenacity value of the membranes. The result of the tensile strength of the membranes shown in figure 3.

Figure 3. Tensile Strength result of (a) PVDF with TiO and (b) PES with TiO.

Based on figure 3 (a) The highest tenacity value of the three samples above is at a 30wt% PES@TiO$_2$ concentration of 0.92%. Then followed by Pure PES 25wt% of 0.78% and PES@TiO$_2$ 20wt%. Whereas in figure 3.2 (b) PVDF@TiO$_2$ shows an increase in value from 0.453 MPa to 0.5 MPa when the specimens with PVDF fiber composition. As a result, the effect of adding TiO$_2$ on PES and PVDF significantly increases the mechanical strength of the membrane, which also influences membrane life [15].

Figure 4. Surface Roughness test result (a)PVDF@TiO$_2$ 10wt% (b) PVDF @TiO$_2$15wt (c) PVDF@TiO$_2$ 20wt%
Figure 5. Surface Roughness test result (a) Pure PES 25wt% (b) PES@TiO2 20wt% (c) PES@TiO2 30wt%.

Surface roughness of each composition of PVDF and PES also shown the different. For the surface roughness structure of PVDF and PES we can see in figure 4 and figure 5. and the measurement of every surface roughness in table 1.

Table 1. PVDF and PES Surface Roughness measurement.

| Membranes                  | $R_a$(nm) | $R_q$(nm) | $R_t$(nm) |
|----------------------------|-----------|-----------|-----------|
| PVDF with TiO, 10wt%       | 11.45     | 13.76     | 65.31     |
| PVDF with TiO, 15wt%       | 19.05     | 24.73     | 122.1     |
| PVDF with TiO, 20wt%       | 30.83     | 38.36     | 155.3     |
| Pure PES, 25wt%            | 21.39     | 27.45     | 126.6     |
| PES With TiO, 20wt%        | 17.22     | 21.88     | 88.37     |
| PES With TiO, 30wt%        | 10.08     | 13.28     | 63.92     |

In table 1 PES@TiO2 20wt% shows the best surface roughness value among others. The PES@TiO2 20wt% mixed membrane identifies that with the modification of the addition of an electric field it can make equal distribution of processes. Whereas in Table 4.2 PVDF@TiO2 10% can reduce the roughness value of the membrane surface compared with other mixed concentrations, this is related to the flux value that has been obtained and the anti-fouling properties of the membrane [16], [17]. The membranes are also working on water treatment performance to see the durability of membranes by fluks measurement of each membrane. The result of performance of water treatment test can seen in figure 6.

Figure 6. Water Treatment Performance Test Results (a) PVDF (b) PES.
In research [18]–[21] states that the results of water permeability or flux from the microfiltration membrane are more than 1000 L/m².h.bar. Where the use of microfiltration membranes is the process of separating suspended solids or bacteria of water. Also completing this is the beginning of the water filtration process before proceeding on the Ultrafiltration membrane process and Reverse Osmosis. The results obtained by the PES membrane are also directly proportional to the above statement with the best results at a concentration of PES@TiO₂, 20wt%, 2558.9 L/m².h.bar. and for PVDF@TiO₂ membranes at a concentration of 10wt% with the highest flux value of 239.41 L/m².h.bar. For the contact angle of membranes also testing to see the degree of membranes can filtering the water the contact angle of PVDF and PES membranes can be seen in figure 7.

![Figure 7](image_url)

**Figure 7.** Contact Angle Test Results of PVDF and PES.

The highest hydrophilicity was found in PVDF@TiO₂ 10wt% which reached 41° then 43° for mixing Pure PES 25wt%. This proves that a mixture of PES and PVDF membranes with the addition of TiO₂ using the electric field method can reach a contact angle that is similar or even lower compared to previous studies [22]–[25].

4. Conclusion
A mixture of PES and PVDF membranes with the addition of TiO₂ was successfully made using the 15000V DC electric field method and showed remarkable results. The results of observations using SEM shows that the morphological structure of the membrane has an equal and fine pore size from low to high concentrations, this is directly proportional to the tensile strength of PES and PVDF membranes, the higher the concentration, the greater the maximum stress obtained. While surface roughness has values related to flux and membrane hydrophilicity. The higher the pure water flux, the lower the hydrophilicity. The value of pure water flux results from the study shows that the addition of TiO₂ and the use of a 15000V DC Electric Field are some of the effective methods to improve membrane capability both in terms of water filtration performance and membrane lifetime.

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