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# THE EFFECT OF TITANIUM OXIDE ON CHARACTERISTIC OF POLYSULFONE MEMBRANE

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## ABSTRACT

*Titanium oxide ($TiO_2$) was introduced into Polysulfone (PS) membrane in order to produce modified PS/$TiO_2$ membrane via phase inversion method. The main objective of the present study is to examine the permeability, hydrophilicity and thermal stability of the polysulfone membrane. The membrane was analyzed using Field Emission Scanning Electron Microscope (FESEM) for surface analysis and contact angle measurement for hydrophilicity test. The effect of different $TiO_2$ concentration on membrane permeability was studied and varies from 0 % - 10 % v/w. The results indicated that higher concentration of $TiO_2$ gave better membrane hydrophilicity based on reduction of contact angle analysis. At 10 % $TiO_2$ concentration, contact angle obtained was 26.8 while at 0 % $TiO_2$ , contact angle value was 44.7. On the other hand, 6 % of $TiO_2$ gave better water permeability of the membrane where the optimum permeation flux at 10 bar and 30 bar pressure using PS/ $TiO_2$ membrane with the addition of 6g $TiO_2$ is 14,337L/$m^2$h and 28, 505 L/$m^2$h respectively. Formation and distribution of the pores on the surface of the membrane also improved with addition of $TiO_2$ as shown in FESEM analysis. In average, large amount of smaller size of pore was obtained when 6 % of $TiO_2$ was added in Polysulfone (PS) dope solution.*

Polymeric membranes are the main choices of immobilization matrix in the enzymatic industry due to their excellent flexibility, stability, separation qualities and toughness [1]. Polysulfone (PS) is one of the preferable polymeric material in membrane preparation due to its low cost, excellent mechanical properties, great chemical and thermal stability and superior film ability [2]. However, this material has hydrophobic characteristics which may affect the flux performance of the membrane due to the membrane fouling. generally, hydrophobic particles tend to cluster or group together to form colloidal particles due to its lowers interfacial free energy or surface tension. Thus for the process application with membrane, hydrophilicity properties play an important role in enhancement of the process involved. Dasgupta et al., [3] reported that fouling process can be reduced using the membranes that has been modified its surface chemistry to render their hydrophilic properties. Various techniques for improvement of membrane surface chemistry has been reported by including application of $TiO_2$ as a coated material to polymer membrane or dispersed of $TiO_2$ in the polymer solution. Rahimpout et al. reported that the addition of $TiO_2$ in the membrane results in better flux but the performance of the flux depend on the $TiO_2$ immersion time in the dope solution. Theoretically, modification of polymer membrane attempts to introduce more COOH functional group and thus increases the hydrophilicity of the membrane surface for deposition of $TiO_2$. The addition of $TiO_2$ particles as addictive in PS membrane is extensively studied due to its ability to produce membrane with better permeability, superior hydrophilicity and improved mechanical and thermal stability [4]. Improvement of the thermal and mechanical stability of the membrane has been extensively reported by Abedini et al. [5] and Rodríguez et al. [6]. The present of $TiO_2$ nanoparticles on the cellulose acetate membrane slightly increased in the thermal stability of cellulose acetate membrane due to the presence of organoclay nanofillers. These studies thereby ascertained the ability of incorporated $TiO_2$ to enhance the thermal resistance of the nanocomposite membranes. Thus in the present study, the optimum composition of $TiO_2$ inside PS membrane is examined by evaluating the characteristics of the membrane in term of the morphology and pore size distribution, porosity, hydrophilicity and permeation flux of the membrane.

PS/$TiO_2$ membrane was prepared using phase inversion method. The composition of PSP/$TiO_2$ dope solution is shown in Table 1. The dope solution was stirred at room temperature for 24 hours. Then, the solution was sonicated for 30 minutes to remove air bubbles. The solution was casted on a glass plate using 200 µm thick casting knife. Afterward, the casted film was immersed in distilled water at room temperature and the membrane was left overnight in water bath to remove an excess of NMP. Then, the membrane was dried at room temperature and stored for further used.

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**Table 1.** Composition of PS/$TiO_2$ dope solution

| Membrane | PS (g) | PVP (g) | NMP(mL) | $TiO_2$(g) |
|---|---|---|---|---|
| 1 | 18 | 5 | 82 | 0 |
| 2 | 18 | 5 | 82 | 2 |
| 3 | 18 | 5 | 82 | 6 |
| 4 | 18 | 5 | 82 | 10 |

Cross section of the membrane was characterized under liquid nitrogen by using JEOL JED-2300 Field Emission Scanning Electron Microscope (FESEM) at 10 kV accelerating voltage on platinum sputter coated sample. Then, the pore size of the membrane was determined manually using the result from FESEM image by calculating the percentage average size of the pores. The membrane was soaked in distilled water for 24 hours. Then, the wet membrane was wiped with bloating paper before being weighed. After that, the membrane was dried at 75ºC for 48 hours. The weight of wet and dry membrane was recorded. The porosity of membrane was evaluated as the function of weight as suggested by Abedini et al. [5], using the Eq.(1):

$$\varepsilon = \frac{(W_{wet}-W_{dry})/\rho_{water}}{(W_{wet}-W_{dry})/\rho_{water}+W_{dry}/\rho_{water}} x100 \quad (1)$$

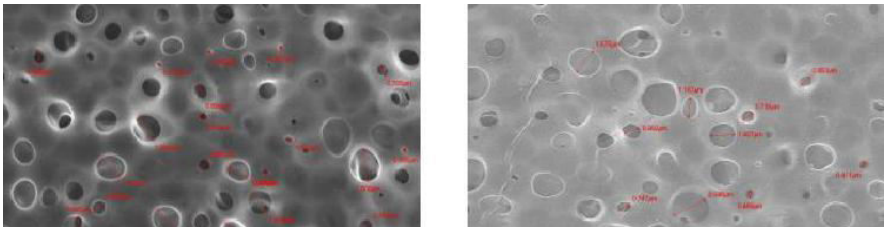
**Surface Tension Measurement.** The surface tension of the membrane was characterized using DropMeter A-100 Contact Angle Analyser. The analysis was done by dropping a droplet of deionized water (6.70µL) onto the surface of membrane that is positioned on top of glass slide. Then, the average value of contact angle was analyzed at five different positions through micrographs.

**Pure Water Flux (PWF).** Pure water flux analysis was done in a batch mode. The tested area was determined to be 23.76 $cm^2$. According to Abedini *et al*. [5], PWF was verified by using Eq.(2).

$$PWF = \frac{Q}{A\Delta T} \quad (2)$$

where Q represent the quantity of permeate (L), A is the effective area of membrane($m^2$) and ΔT is the sampling period (h).

**Morphology Analysis of PS/$TiO_2$ Membrane.** Field Emission Scanning Electron Microscope (FESEM) was used to observe the effect of $TiO_2$ on PS membrane morphology. Figure 1 shows that the amount of small pore size increased as the $TiO_2$ concentration was increased. The image shows that the formation of the pore size at surface the membrane matric as it is essential in order to retain immobilized enzymes at its position and provided larger surface area for better enzymatic activity. According to Eldin et al [6], membranes endowed with the smallest pores are more active. The reason for this behavior is still related to the circumstance that the membranes endowed with smaller pores have a greater surface available for reaction and, consequently, for enzyme attachment.



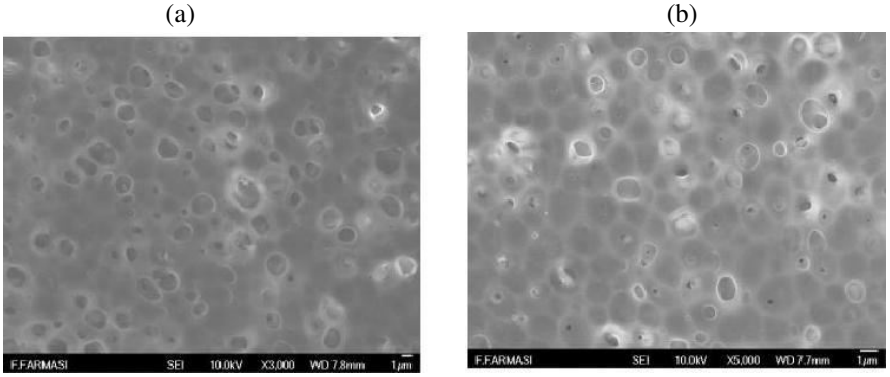



**Figure 1.** FESEM micrographs of PS/$TiO_2$ membrane (a) 0g $TiO_2$ (b) 2g $TiO_2$ (c) 6g $TiO_2$ (d) 10g $TiO_2$.

In addition, Figure 2 shows the macroviod formation is increased as the increase of $TiO_2$ concentration in the modified PS/ $TiO_2$ membrane. The increase in the viscosity of the dope solution decelerate the exchange rate of solvent/nonsolvent during membrane formation. This condition will interrupted the demixing process in the coagulation bath that will then leads to the formation of macrovoids [1]. Formation of macrovoid structure also provides effective environment for diffusion of enzymes [7].

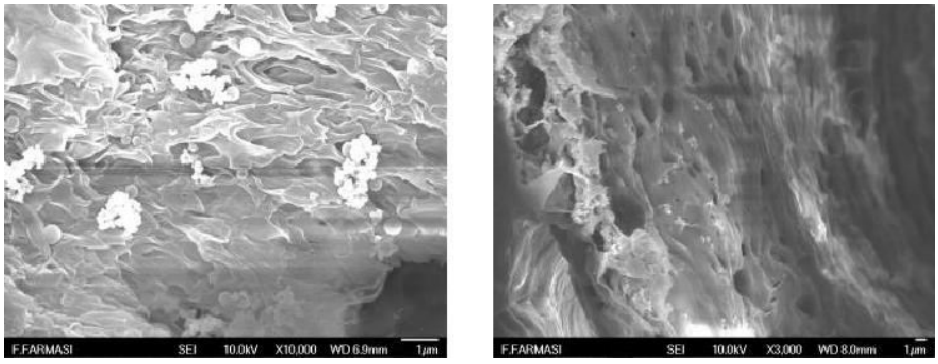



**Figure 2.** Cross-section of PS/$TiO_2$ membrane (a) 2g $TiO_2$ (b) 10g $TiO_2$.

**Pore Size Distribution.** The pore size distribution analysis of the fabricated membrane with and without addition of $TiO_2$ was determined as revealed in Figure 3. The results shown that the size of the pore formed distribute between 0.5µm to 3µm. Addition of the $TiO_2$ in the membrane formulation formed smaller size of the pore and most of the pore size formed was smaller than 2µm. From the results, it shows that the addition of 10 g $TiO_2$ give higher amount of pore with the size of 0.5 µm. Similar pattern is observed for membrane with addition of 2 g $TiO_2$. While addition of 6 g $TiO_2$ results in the highest pore with the size of 1.1 µm. On the other hand, membrane

without addition of $TiO_2$ give higher pore with an average size of 1.5 µm. This results indicates that the present of $TiO_2$ in preparation of membrane capable to form a smaller size of the pore. Whereas in term of consistency of the pore size, 6 g $TiO_2$ results in optimum pore with an average size of 1.1 µm, which desires for better enzymatic performance. The increase number of small pore size is due to the surpress of the pores by $TiO_2$ particles which reduce the actual size of the pores [8].

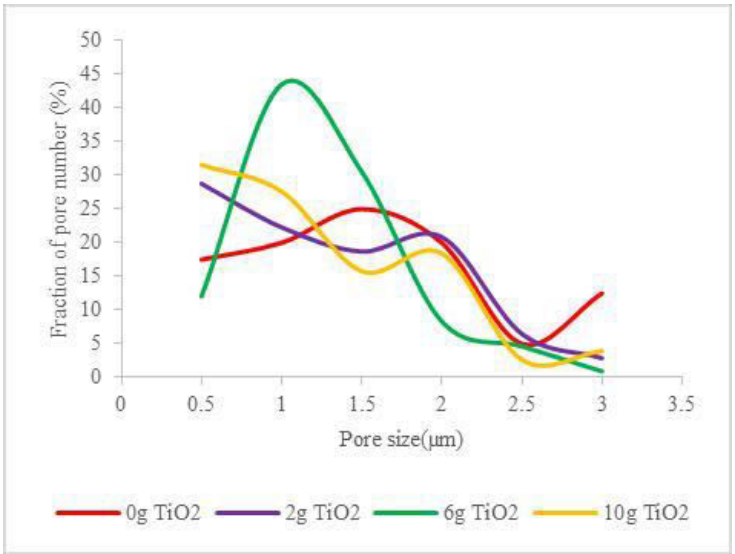



**Figure 3.** Pore size distribution of PS/$TiO_2$ membrane.

**Porosity of the membrane.** Table 2 shows the porosity of PS/ $TiO_2$ membrane. It can be observed that the porosity of the membrane increase due to the increase of $TiO_2$ particles amount present inside the membrane. The increase in porosity of membrane can be observed with the addition of $TiO_2$ as it slightly increase from 75.19% to 75.27% by the addition of 2g of $TiO_2$. On the other hand, the increase amount of $TiO_2$ inside dope solution also shows a considerable changes in the porosity of the membrane as it increase from 75.27% of 2g addition of $TiO_2$ to 77.13% of the addition of 10g of $TiO_2$. During precipitation process of wet-casting polymeric membrane, stress accumulated between polymeric substances and $TiO_2$ particles because of the shrinkage of organic phase [1]. This phenomena leads to the formation of pores. When there is higher amount of $TiO_2$ particles present, the stress becomes greater and causing the formation of higher porosity membrane.

**Table 2.** Porosity of PS/ $TiO_2$ membrane

| Amount of $TiO_2$(g) | Porosity (%) |
|---|---|
| 0 | 75.19 |
| 2 | 75.27 |
| 6 | 79.49 |
| 10 | 77.13 |

**Hydrophilicity Analysis.** The hyrophilicity of the membrane can be verified through contact angle measurement. The reduction of the contact angle signifies the increase in the hydrophilic properties of the membrane [9]. Table 3 shows the effect of addition of $TiO_2$ in the PS membrane modification. The hydrophilicity of the membrane is proven to be enhanced in the presence of $TiO_2$ particles from 44.7º to 38.7º with the addition of 2g of $TiO_2$. Moreover, further addition of $TiO_2$ into the casting solution also has proven to reduce the contact angle from 38.7º to 26.8º with the addition of 10g of $TiO_2$.This is because $TiO_2$ contains extreme hydrophilic traits which consist of vast amount of hydroxyl group. This hydroxyl group is responsible for the transformation into hydrophilic characteristics of the membrane [1]. In the presence of $TiO_2$ particles, the surface of the membrane is exposed to low pH hydrochloric acid causing partial hydrolysis to occur and transforming the hydrophilic properties of the

membrane.

**Table 3.** Contact angle of PS/ $TiO_2$ membrane

| Amount of $TiO_2$(g) | Contact Angle (°) Right | Left | Contact Angle Average (°) |
|---|---|---|---|
| 0 | 43.3 | 46.1 | 44.7 |
| 2 | 37.5 | 39.9 | 38.7 |
| 6 | 38.2 | 33.8 | 36.0 |
| 10 | 29.3 | 24.3 | 26.8 |

**Permeation Flux of Membrane.** Figure 4 shows that the pure water flux for three different pressure that are 10, 20 and 30 bar. The result reveales that the PWF increases as the increases in pressure from 10 bar to 30 bar. Moreover, the results also reveales that the PWF increases as the increases amount of $TiO_2$ present inside the membrane from 0g to 6g of $TiO_2$. The optimum permeation flux at 10 bar and 30 bar pressure is obtained by PS/ $TiO_2$ membrane with the addition of 6g $TiO_2$ that is at 14,337L/$m^2$h and 28, 505 L/$m^2$h respectively. Conversely, at 20 bar pressure, the optimum flux was obtained by PS/ $TiO_2$ membrane with 2g of $TiO_2$ which was at 17,600 L/$m^2$h. This trends occurred due to the increases in the porosity and pore size distribution of PS/ $TiO_2$ membrane. Additionally, the flow rate also increases due to the increases of hydrophilic properties of the membrane as referred to Table 3. In general, it can be concluded that the permeability of the membrane depends on the porosity and pore size of the membrane [5]. However, the PWF for 10g $TiO_2$ is low compare to the other PS/ $TiO_2$ membrane. The high concentration of $TiO_2$ particles inside dope solution causing it to be viscous and eventually slow down the demixing process of PS/ $TiO_2$ membrane formation. This phenomena create thicker layer of skin in the upper and lower part of the membrane and formed complex structures of pores within the membrane dimension containing higher amount of $TiO_2$ particles blocking each pores [9]. This condition makes the pure water unable to pass through the membrane at higher flowrate even though there are many pores present within 10g $TiO_2$ content of PS/ $TiO_2$ membrane.

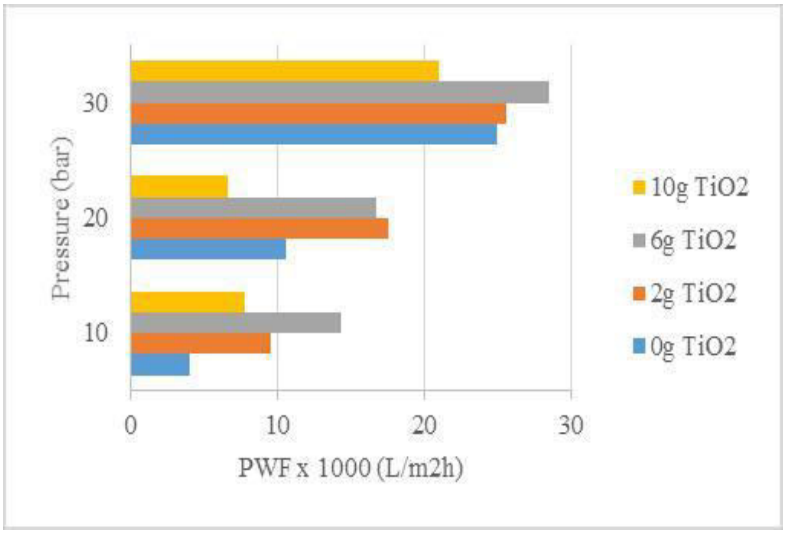



**Figure 4.** Permeate flux for PS/ $TiO_2$ membrane at 10, 20 and 30 bar.

In this research, PS membrane was modified with the addition of $TiO_2$ particles at composition of 0g, 2g, 6g and 10g. The membrane prepared by phase inversion method was characterized for surface area analysis, pore size distribution, porosity analysis, hydrophilicity analysis and pure water flux analysis. The FESEM observation reveals that small size of the pore was obtained and the number of the pore with smaller size increased as the amount of $TiO_2$ particles inside the membrane was increased. This is supported by pore size distribution analysis that shown the range of pore between 0-3µm. In addition, contact angle analysis indicated that the hydrophilicity of PS membrane was improved with addition of $TiO_2$ particles. This study was in agreement with the results from

permeation flux analysis. Permeation flux of the membrane consist of $TiO_2$ particles increased as the concentration of $TiO_2$ in the membrane increased.

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