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The Effect of TiO2 Particles Addition on the Characteristics of Polysulfone Membrane

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***Abstract*— This study aimed to characterize the modified Polysulfone-TiO_2 membrane via hydrophilic character, the molecular weight cutoff of the membrane and surface morphology of the membrane. Flat sheet modified Polysulfone membrane was prepared by using the phase inversion technique. N-methylene-2-pyrrolidone (NMP) was used as a solvent to dilute Polysulfone pellets. Titanium dioxide (TiO_2) and polyvinylpyrrolidone (PVP) were added to enhance the hydrophobic character of the Polysulfone membrane. The hydrophilic characteristics of the modified Polysulfone-TiO_2 membrane were analyzed by contact angle and were compared with conventional Polysulfone membrane. It was found that the addition of TiO_2 in Polysulfone membrane has improved the hydrophilic performance of Polysulfone membrane toward water flux. The membranes also were tested with a molecular weight cut off (MWCO) using different weights of polyethylene glycol (PEG) which are 200, 400, 600 and 1000 Da. For membrane with the addition of TiO_2, a decreased in pore sizes was determined. The membranes also were analyzed under scanning electron microscope (SEM) to determine the morphology of the surface and cross-section. It was found that pore sizes of Polysulfone with TiO_2 membrane have become smaller, which contain more nano in size and formation of finger-like voids compared to the Polysulfone membrane.**

***Keywords*— titanium dioxide; polysulfone; hydrophilic; molecular weight; morphology**

I. Introduction

The addition of titanium dioxide (TiO_2) particle in Polysulfone membrane is one of the alternatives in solving the known limitation of Polysulfone which is a hydrophobic character. Polysulfone membrane was widely applied in the industry especially involved with ultrafiltration as it has multiple advantages such as high mechanical strength, high rigidity, natural film-forming, good resistance toward temperature, chemical stability as well as wide pH value range (pH 2 – 12) [1], [2]. The hydrophobic Polysulfone has been improved by using hydrophilic material especially inorganic material as this kind of material provides more convenient operation and gives a stable effect [2].

TiO_2 has become one of the most active inorganic material which provides a super-hydrophilicity and other advantages such as non-toxic, good compatibility with organic solvents used in dope solution, anti-decomposing-bacterial and UV-resistance (1). Since TiO_2 has offered good advantages, it has been applied widely in catalysts, sunscreens, cosmetics, coatings [3] as well as food packaging applications [4]. The hydrophilicity of TiO_2 can alter the hydrophobic Polysulfone after it has been treated by anionic surfactant sodium dodecyl sulfate (SDS) [2].

To improve the membrane performance, the surface porosity of the Polysulfone membrane needs to improve by the presence of the nanoparticle, TiO_2 [5]. The asymmetrical Polysulfone membrane which consists of dense skin and porous layer has been thickened with TiO_2 concentration. Thus, in the present study, the effect of TiO_2 particles on the different formulation of Polysulfone membrane was investigated. Less research was reported on the effect of TiO_2 on the different formulation of Polysulfone membrane. The effect of the addition of TiO_2 in Polysulfone membrane was analyzed by determining the hydrophilicity of the membrane, the pore size of the membranes via molecular weight cutoff (MWCO), and also surface image under scanning electron microscope (SEM).

II. Material and Method

A. Material

Polysulfone pellet (Mw ≈ 35,000 g/mol) was bought from Sigma Aldrich, 1-methyl-2-pyrrolidone (NMP) was purchased from Merck, polyvinylpyrrolidone (PVP) K30 in powder formed was purchased from Sinopharm and titanium dioxide (TiO2) in powder formed was purchased from R&M Chemicals.

TABLE I
CONTACT ANGLE OF POLYSULFONE, POLYSULFONE-PVP, POLYSULFONE-TIO_2 AND POLYSULFONE-PVP-TIO_2 MEMBRANE

Type of membrane	Contact Angle (^{0}) Right	Contact Angle (^{0}) Left	Contact Angle (^{0}) Average
Polysulfone	72.1	73.1	73.0
Polysulfone-PVP	60.7	57.8	59.3
Polysulfone-TiO_2	70.1	69.3	69.7
Polysulfone-PVP-TiO_2	60.3	57.3	58.8

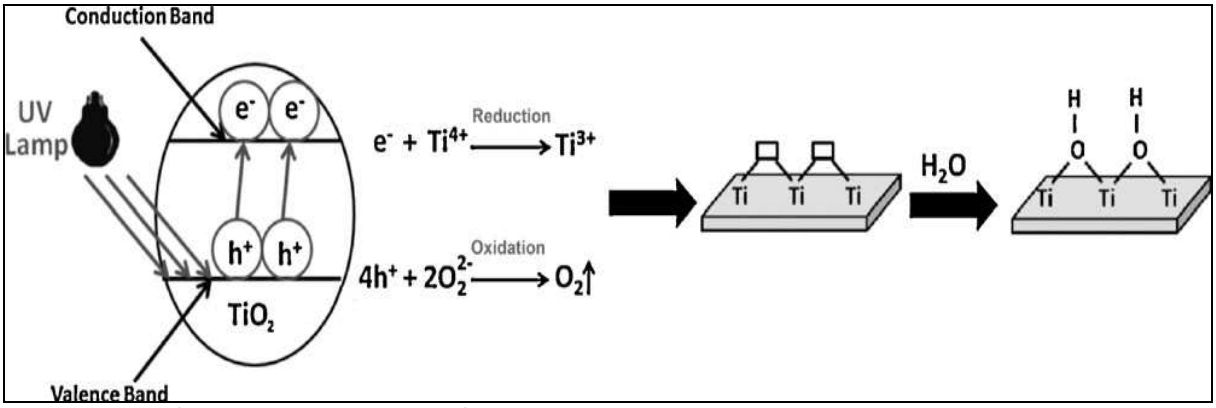


Fig. 1 Mechanism of TiO_2 hybrid on the substrate surface [12]

B. Methodology

The dope solution was formed by using weight percent ratio. A solution was prepared by mixing 17.0 wt % of polysulfone with 83.0 wt % of the NMP and also the additives (PVP and TiO_2) [6]. The Polysulfone was mixed with NMP to form a dope solution and continuously stirred for 24 to 48 h at 60 ˚C to achieve a homogeneous solution. Then about 1.5 wt % of the additive, TiO_2 was added into the dope solution and continuously stirred for 8 h at the same temperature for a homogenous solution. The homogeneous solution was then added with 3.0 wt % of PVP and stirred for another 5 h at the same temperature. This method also was used [7], [8]. The homogeneous solution was then cast by using a casting machine based on the phase inversion technique. A thickness of the membrane was set around 100 µm [9]. The flat sheet membranes were then soaked in distilled water for 24 h and dried at room temperature for another 24 h [9].

C. Membrane Analysis

Contact Angle Measurement Instrument analysis was used to measure the contact angle needed to identify the change in the hydrophilic character of the membrane. The contact angle between the water and solid membrane was directly measured by contact angle measurement instrument, Wafer Surface Analysis System (VCA 3000, AST products. INC, USA) [6], [10]

Molecular Weight Cut Off (MWCO) was used to identify the size of pore membrane. The MWCO analysis was conducted using Polyethyleneglycol (PEG) with different molecular weights (200, 400, 600 and 1,000 Da). The analysis was conducted by using the membrane filtration rig with constant of PEG concentration, 50 ppm. The filtration experiment was carried out using a flat sheet membrane with a surface area of 17.63 cm2, and the applied pressure was constant at 4 bar. The method was used [11], but it has been modified based on the condition of the membrane.

Scanning electron microscope (SEM), (HITACHI TM3000 Tabletop Scanning Electron Microscope, Hitachi High Technologies America, Inc.) image was used to identify the morphology of the surface and cross-section for the membranes. Before undergoing SEM analysis, the membranes were coated with gold for about 60 seconds to remove any residual ions on the membranes. The surface image of membranes was analyzed under 10.0k magnification while the cross-section image was captured under magnification of 1.5k [8].

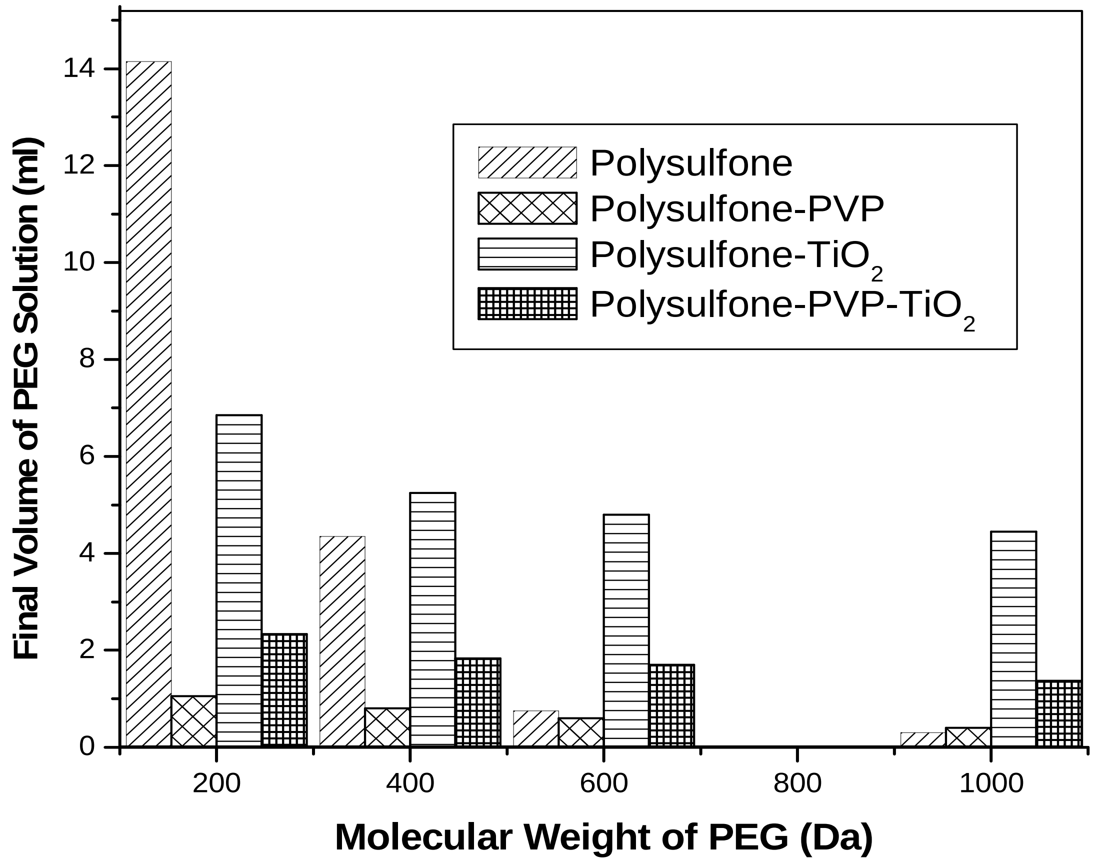


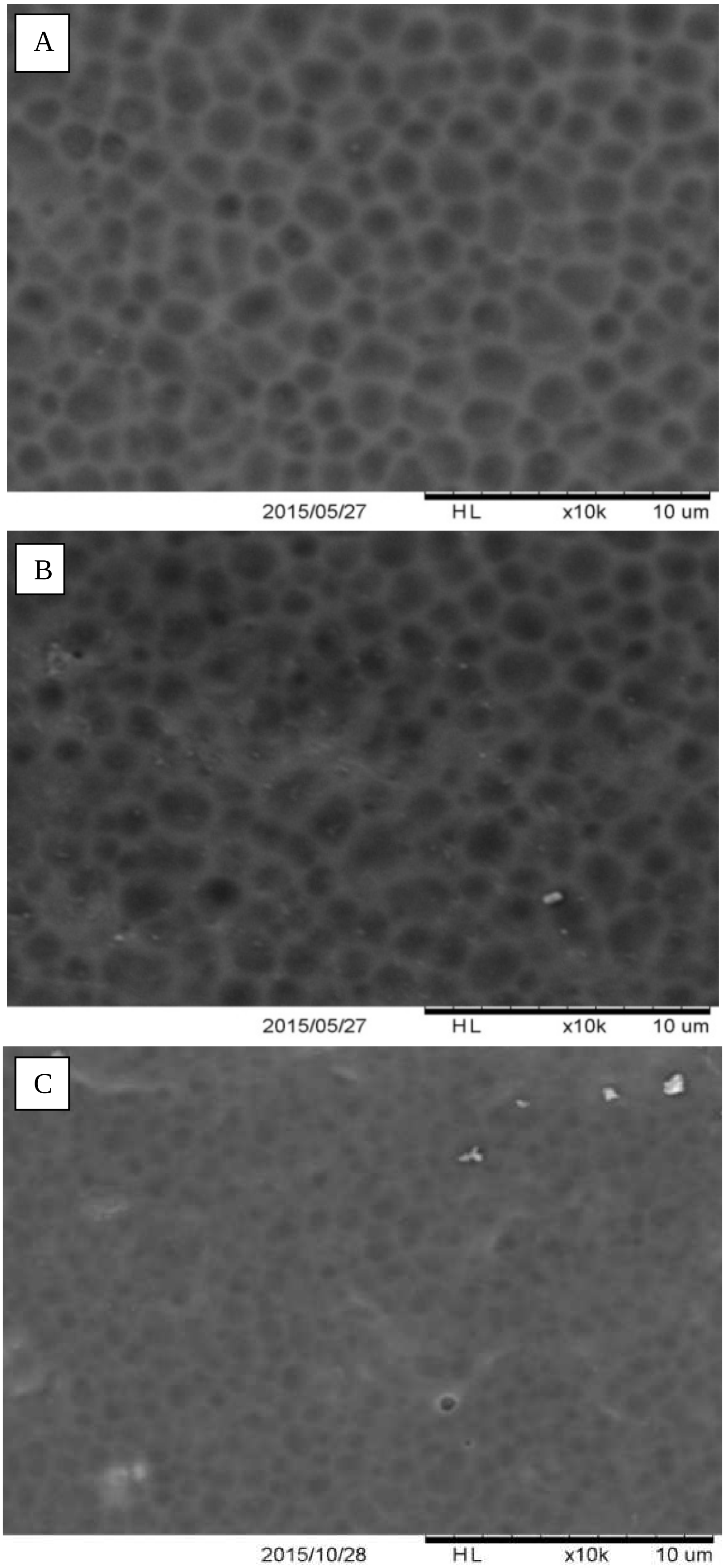
Fig. 2 Final volume PEG solution versus PEG molecular weight between Polysulfone and modified Polysulfone membrane

III. Results and Discussion

Water contact angle data for Polysulfone and modified Polysulfone membranes are summarized in Table 1. The result indicates that the Polysulfone-PVP-TiO_2 membrane was more hydrophilic as compared to Polysulfone membrane. The addition of PVP and TiO_2 in Polysulfone increased the hydrophilic character to the membrane. The addition of hydrophilic TiO_2 in Polysulfone solution has promoted diffusion of water from water coagulation bath to the cast polymer membrane, and lead to the development of long finger-like voids as well as enhanced overall porosity of the membrane [9]. The modified membrane with TiO_2 particles, can attract water molecules and thus reduced the angle of water droplet [1]. The addition of TiO_2 in the membrane will hybrid the membrane with increasing hydrophilic characters [12]. Moreover, the hydrophilic property was influenced by the surface area of the nanoparticle (TiO_2) which was as higher nanoparticle surface area leads to higher adsorption of water molecules [13]. A mechanism of TiO_2 hybrid on the Polysulfone membrane is shown in Figure 1. TiO_2 provides a route for the molecular water to be degraded when they pass through it [14]. The affinity of water toward this compound is a sign of hydrophilic character. Thus, the addition of TiO_2 will enhance the performance of the Polysulfone membrane toward hydrophilic character and increase the water flux.

Molecular weight cut off (MWCO) of Polysulfone and modified Polysulfone membranes was tested by using several PEG concentrations which are 200, 400, 600 and 1,000 Da and the results are shown in Figure 2. PEG molecules have been widely used to determine MWCO of the membranes since the PEG is a virtually uncharged macromolecule [15]. The graph in Figure 2 shows a similar decreasing trend in the final volume of PEG sthe olution versus PEG molecular weight. A PEG molecular weight increased the permeability via the membrane becomes harder. The result indicates that 200 Da of PEG can quickly pass through all types of membranes as compared to 1,000 Da of PEG. For Polysulfone membrane, it clearly shows the pore size of the membranes was comfortably in the range of 200 – 400 Da as PEG 200 and 400 Da can pass through the membrane, but 600 and 1,000 Da are hardly diffuse. However, the modified membrane with the addition of TiO_2, the pore sizes might be smaller as only Polysulfone membrane with 200 Da can permeate. MWCO may be a starting point in understanding natural organic matter rejection and other solute separations by membrane filtration, which is the central rejection mechanism of the membrane due to the pore size of the membrane [16]. The MWCO can be defined based on 90% of molecular weight rejected by the membrane.

Scanning electron microscope (SEM) image for Polysulfone and modified Polysulfone-TiO_2 were captured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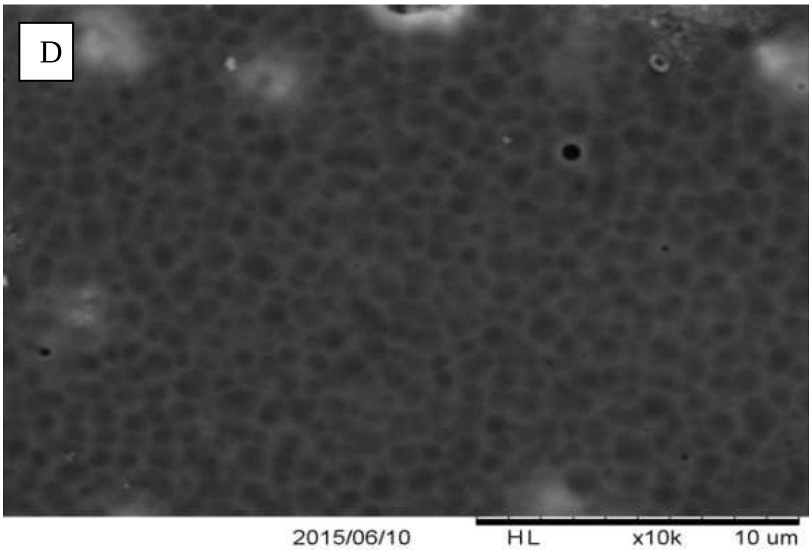
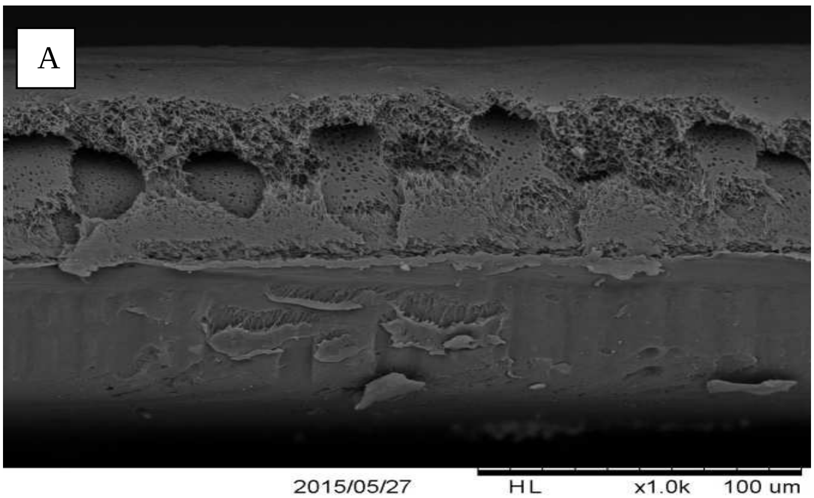


Fig. 3 SEM images of A) Polysulfone B) Polysulfone-PVP C) Polysulfone-TiO_2 D) Polysulfone-PVP-TiO_2 membranes under 10k magnification

Under 10.0k magnification, as shown in Figure 3. The images indicate that Polysulfone membrane has a big topography image. This might happened due to the less polymer concentration in the dope solution will lead more volume of solvent left behind as pores and thus resulted in large of pore size [17]. While for Polysulfone with the addition of TiO_2, the topography image is smaller. The addition of TiO_2 in Polysulfone solution can be verified as an agglomeration of small white spots on the surface of the membrane as shown in Figure 3C and 3D [9]. The TiO_2 particles attached to the Polysulfone could be due to the combined effects between chemical and physical interactions. TiO_2 was used to increase the porosity of membrane as absorption has occurred between hydroxyl on the surface of the TiO_2 particle with Polysulfone molecular chains [2]. Furthermore, TiO_2 particles also increased the specific area of the membrane by stabilizing the macromolecule network structure. Thus, the addition of TiO_2 particles has enhanced the surface morphology of the Polysulfone membrane by decreasing the pore size of the membrane as well as increase the surface area of the membrane.

Moreover, Figure 4 shown SEM images for the cross-section of Polysulfone, Polysulfone-PVP, Polysulfone-TiO_2 and Polysulfone-PVP-TiO_2 membrane under same magnification. The void of Polysulfone with the addition of PVP and TiO_2 was a long finger-like compared to the Polysulfone membrane. The combination of PVP and TiO_2 in the dope solution helps to enhance the development of long finger-like voids as well as increases the porosity of Polysulfone membrane. The formation of the finger-like void was assisted by TiO_2 which has hydrophilic character and encourage diffusion of water into the dope [18], [19]. Thus, this indicates that the addition of TiO_2 had changed the morphology of the Polysulfone membrane and capable of enhancing the performance of the membrane.



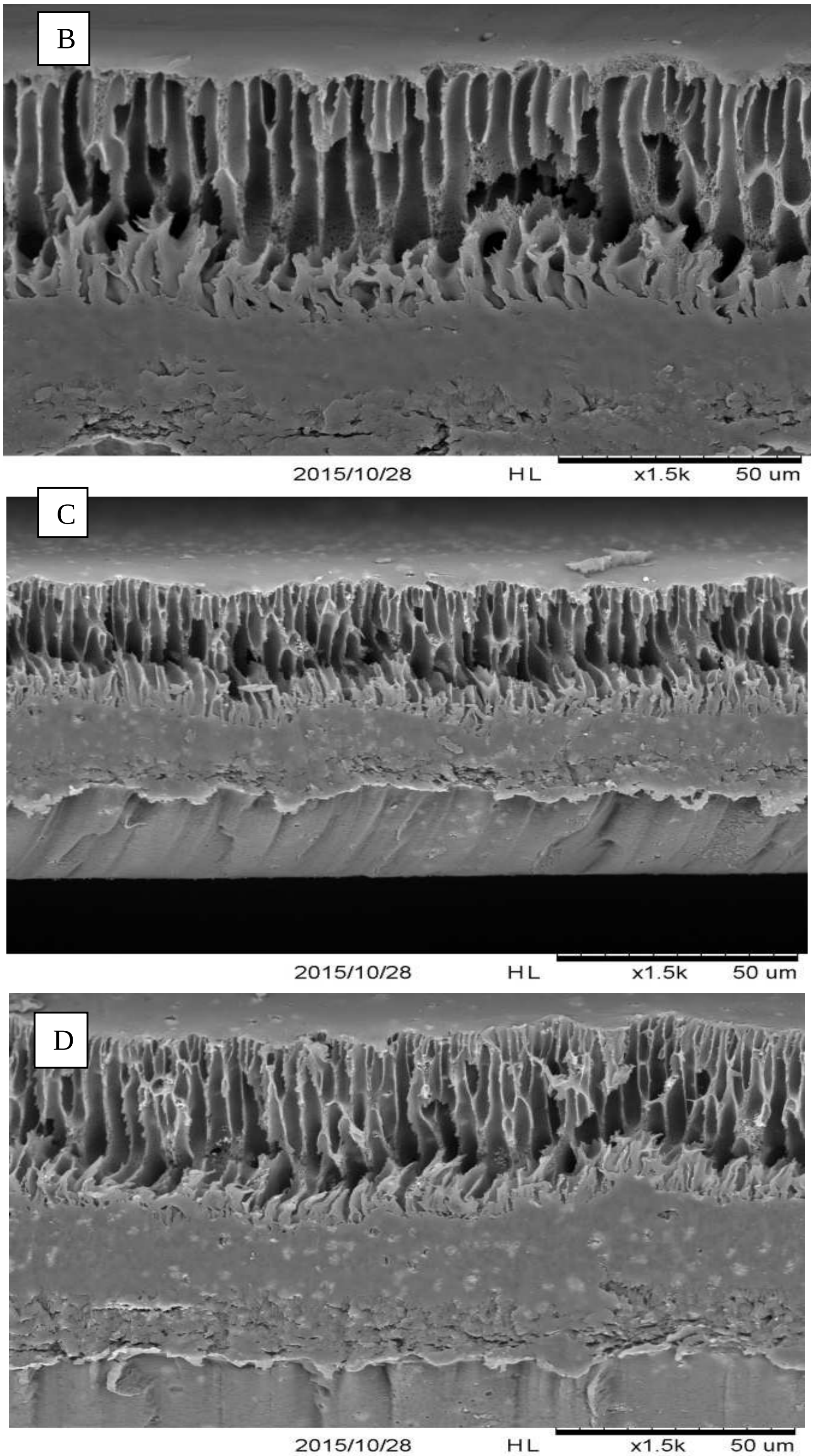


Fig. 4 SEM images of A) Polysulfone B) Polysulfone-PVP C) Polysulfone-TiO_2 D) Polysulfone-PVP-TiO_2 membranes under 1.5k magnification

IV. Conclusions

With the addition of TiO_2 particles, the characteristics of Polysulfone membrane were improved. The result indicates that present of TiO_2 particles in the membrane gave the higher hydrophilic character as the angle of water contact decreased. The Polysulfone-TiO_2 was able to permeate more PEG solution under various PEG concentrations as compared to Polysulfone membrane. The presence of TiO_2 in Polysulfone membrane produces a higher surface area, and moreover, The pore size of the membrane was more evenly distributed compared to the Polysulfone membrane. The finger-like voids also were formed with the presence of TiO_2.

Nomenclature

Dalton	Da
Weight percent	Wt %
Hour	h
Part per million	ppm
Area	cm^2
Degree	°
Milliliter	ml

Subscripts

TiO_2 Titanium dioxide

M_w Molecular weight

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