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# Effect of Polyaniline on Surface Properties of Polysulfone Membrane

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This study investigates the effect of Polyaniline (PANI) on surface properties of Polysulfone (PSf) membrane. The membrane was prepared via phase inversion method at high concentration of PANI (0-15 wt.%). The membrane was characterized in term of morphology, surface roughness and porosity. The result showed that by mixing PANI in PSf membrane, the surface roughness increased up to 84%. This result indicate that addition of PANI improve surface hydrophilicity of membrane. Furthermore, the membrane porosity was enhanced in the presence of PANI. This result is in line with morphology properties which found that PANI act as incompatible filter in PSf matrix which enhanced membrane porosity and surface roughness. Although PANI is incompatible but based on membrane surface hydrophilicity, PANI has potential to be used as an additive in membrane fabrication.

## 1. Introduction

Water is the most important human need in life. However, due to the quick development of total populace, mishandle of water assets and water pollution, the problem of water shortage increasing drastically.
Hence, cost-effective technologies must be developed to extend water resources and solve water pollution problems. Membrane water treatment is expected to play an increasingly important role in areas such as drinking water treatment, brackish and seawater desalination, and wastewater treatment and reuse, because it is simple in concept and operation, does not involve phase changes or chemical additives, and can be made modular for easy scale up (Harun et al., 2013)
Membrane filtration is one of the advance methods which is reported to be able to separate humic acid efficiently. Sathish Kumar et. al. (2015) reported that the water treatment using generally have more advantages as compared to ordinary water treatment process to separate humic acid. This is due to only required small spaces and less energy consumption. However, Yunos et al. (2013) reported that the selection of membrane material which can produce high permeability removal is very challenging. Ultrafiltration (UF) is a common well-developed separation process used in water and wastewater treatment, reverse osmosis pre-treatment, and separations in food, chemical and biochemical industries. This process reported able to reduce carbon footprint as compared to conventional method such as flocculation, coagulation and sand filtration method. As a consequence, the improvement of UF process performance is gaining strong attention due to increased demands.
The common polymer such as polysulfone (PSF) and Polyethersulfone (PES) are widely used because it has good mechanical strength, better chemical resistance, high thermal stability, and film-forming property. The membrane always follows trade-off effect whereby high rejection will result low permeability rates. However, the major bottleneck usage of these materials is hydrophobic property. Hydrophobic surfaces are more inclined to fouling which reduce membrane permeability overtime (Shohur et al., 2013).

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In recent decades, there are a lot of researches on improving membrane surface to reduce membrane hydrophilicity. The membrane surface modifications utilizing grafting, plasma, and blending technique with hydrophilic polymer or nanoparticle were produced with excellent result (Jamalludin et al., 2013). Among those techniques, polymer blend is less complicate method to improve membrane separation. The design of polymer blends constitutes an interesting alternative to improve membrane hydrophilicity. It is reported that the cost of membrane blending is quite reasonable and it is free from time-consuming procedures.
In order to improve hydrophilic property and permeability of PSf membrane, hydrophilic PANI was blended together with PSf membrane to undergo water ultrafiltration process in this research. In addition, PANI has high potential to be blended in PSf membrane due to its low cost, adequate level of electrical conductivity and excellence environmental stability (Jaymand, 2013). However the influence of PANI at high concentration of PSf membrane rarely being investigated. Thus, in this study the influence of PANI in PSf membrane was investigated and characterized.

## 2. Details Experimental

### 2.1 Materials and Procedures

In this study, Polysulfone (PSf) has been used as the base polymer in the membrane casting solution. N-methyl-2-pyrrolidone (NMP) acts as the solvent without any purification. The additives that have been used are Polyaniline (PANI) and Polyethylene glycol (PEG). The concentrations of PANI used are as follows: 0 wt. %, 5 wt. %, 10 wt. % and 15 wt. %.
The flat sheet membranes were prepared by phase inversion method. The dope solution was poured on a glass plate and the casting process occurs on the glass plate using a casting steel knife. In order to get wet thin films on average 0.10 μm to 0.14 μm thickness, the membrane was exposed to air for 30 s, and immersed in a coagulation bath of distilled water for a few seconds. All of the membranes were prepared under environmental humidity of 60 % at room temperature of 25 °C.

### 2.2 Membrane Evaluation

The characterization of PANI membrane was conducted by using four different tests on the samples. At this stage, the sample of membrane went through each test and the performance of it was clearly seen after the result came out. Each test has shown variety of different features at each sample. Below are some general explanations about the test for tis membrane.
E-100 Park system of AFM machine was used to measure membrane surface roughness. Apart from that, AFM machine help for better understanding about the effects of additives in membrane towards membrane characterization and performance. Membrane sample was prepared by cutting the sample into 1 cm x 1 cm in size and then placed on the scanner tube. Membrane surface was scanned by 5 μm x 5 μm size. The value of average surface roughness then was recorded.
Scanning Electron Microscopy (SEM) had been used to observe images morphology of the cross-section on the membrane. SEM/EDS model JSM 6380LA was used in this study. It have magnification range of 5,000-50,000 and operates at 2.0 kV – 5.0 kV of accelerating voltage. Firstly, the samples of the membrane were prepared with the sample size about 3 cm x 1 cm. The observations were carried out to see the cross section of the membrane. To get the view for the cross section part, the samples were immersed in the liquid nitrogen. By immersing the samples into the liquid nitrogen, it helped the membrane to easily break. The cross section part that was scanned is at the fracture area. Then, the samples were attached on the plate and coated with platinum coater using a sputter coater to make the membrane become conductive.
Perkin Elmer FTIR Spectrometer 100 is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". This machine can identified unknown materials, determine the quality or consistency of a sample and determine the amount of components in a mixture. Specimen was prepared by cutting the cast film of flat sheet membrane into pieces. The surface of membrane was examined by FTIR spectroscopy to investigate the chemical bonding in membrane structure.
The porosity of the membrane was determined in wet and dry condition. The membrane was cut into 2 cm x 2 cm sample size for all four samples. Each sample was measured three times using three different membranes. Firstly, the membrane was soaked in distilled water for 24 hours at room temperature. After that, wipe the wet membrane gently. Then, the thickness and weight of the wet membrane was measured. After completed the measurement, the samples were dried by leaving it in the oven at 60 $^{o}$C for another 24 h. Finally, the weight of the dry membrane was measured.

$$\text{Porosity, } \varepsilon = \frac{W_w - W_d}{\rho_w \times V} \quad (1)$$

Where $P_w$ is the density of the pure water at room temperature (g/cm$^3$) and V is the volume of the membrane in wet state (cm$^3$).

## 3. Results and Discussion

### 3.1 SEM Analysis

Figure 1 shows the cross section of membrane at different concentration of additives. As shown in the figure, the fabricated membranes had an asymmetric structure that consists of dense skin layer in the top surface of the membrane which functions as barrier for separation purposes. Meanwhile, the sub layer in the middle of the cross-section is to support membrane strength. The large macropores at the bottom can be observed in the figure which is generally for permeate water drainage.

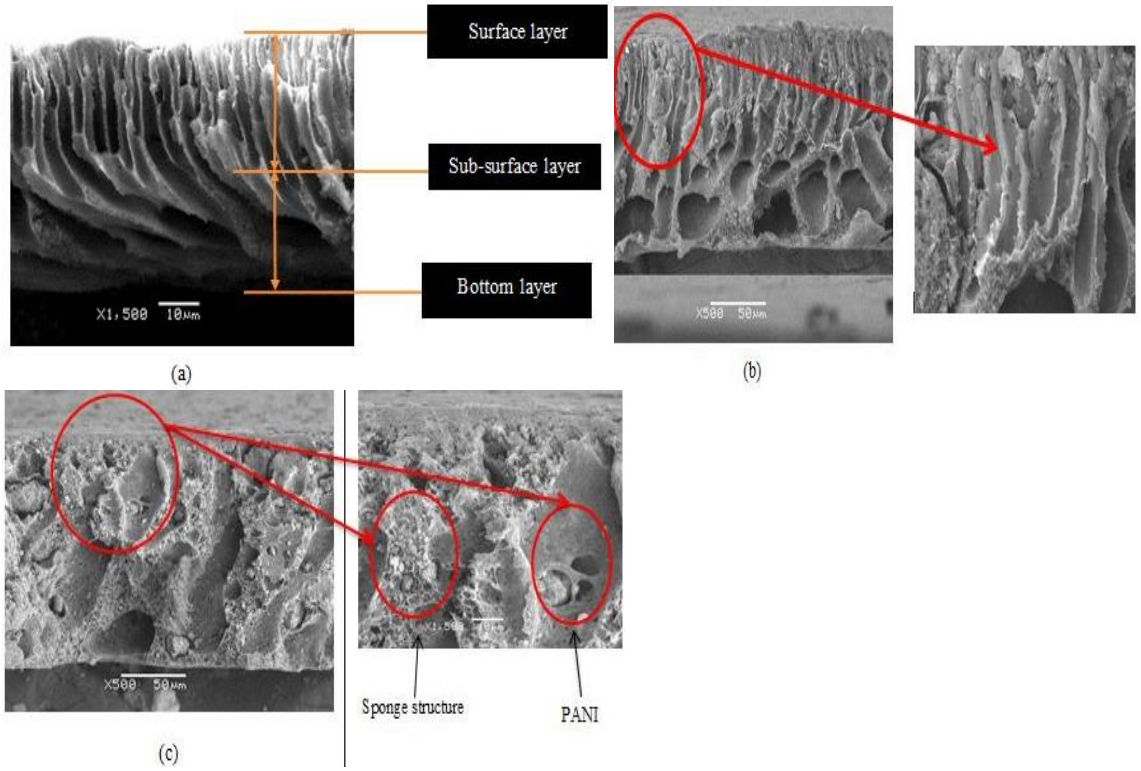


*Figure 1: Cross section of membrane using SEM*

It can be observed that the membrane structure has become different when PANI is added into the dope solution. The addition of PANI leads to a more porous sub layer with larger irregular finger like pores. Furthermore, the thickness of a dense skin layer drastically decreased with increased of PANI content from 5 wt.% up to 15 wt.%. In the figure, sample with the presence of PANI (sample 3 and 4) shows that there is no continuous phase of PANI in the membrane. It can be observed that PANI act as fibre in membrane and increases membrane pores. This behaviour might be due to incompatibility between PANI and PSF which is proven by FTIR result. Apart from that, sponge-like structure on the membrane wall also increased which can be observed Figure 1(c). The formation of large sponge-like structure decreased the solubility of polysulfone in NMP due to the presence of PANI. According to the second law of thermodynamics in every real process, the sum of the entropies of all participating bodies is increased. Thus the addition of PANI reduces the thermodynamic stability and form rapid phase inversion process. This rapid phase inversion process creates large pore and sponge-like structure in membrane as reported by Razali et al. (2014). Although the pore structure increase, PANI seem trapped on the membrane which block the pores of membrane as shown in Figure 1(c). The result will influence the permeability and rejection properties of membrane. Thus the amount of PANI is suggested to reduce in order to decrease this behavior.

According to Sathish Kumar et al. (2015) PSf/PANI substrates exhibit more and larger surface of pore due to the incorporation of PANI. As compared to their work, the finger-like structure of the blended membranes had

good interconnection and thin surface layer especially the membrane in Figure 1(b). This behaviour will increase permeability properties of membrane.

### 3.2 FTIR Analysis

The chemical structure of PANI, PSf/PANI and PSF are analysed using FTIR spectroscopy and the result as shown in Figure 2. This experiment was conducted in order to prove the existence of additive in the membrane.

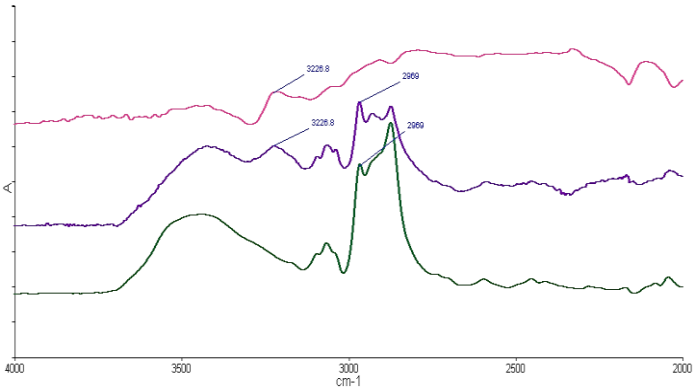


*Figure 2: FTIR analysis*

From Figure 2, it can be clearly seen the peak at 3,226.8 $cm^{-1}$ is present in PANI and PSf/PANI membrane. This peak was assigned to N-H bond which is generally representing amine group from PANI. It also can be observed that this peak is not change even though PANI were diluted using NMP and mixed with PSf. Thus, it is clearly shows that PANI and PSf did not form any interaction during phase inversion. This result is in line with SEM results which PANI did not melt together with PSf and does not form any continuous phase in membrane formation. Although PANI does not form any interaction between PSf, the presence of N-H peak in blended PSf/PANI able to reduce membrane hydrophilicity since N-H bond is polar bond.

### 3.3 AFM Analysis

Figure 3 depicted the 3D roughness surface of membrane. It is worth to mention that the dark colour in the image represent valley and bright colour represent peak of membrane surface. The peak of membrane in sample 4 is increase up to 80.24 nm as compared to pristine membrane which only up to 12.64 nm. This rough peak might be due to presence of PANI on membrane surface which at the same time block or reduce the membrane pores

### 3.4 Porosity Analysis

The porosity in membrane is the most important characteristic. This is due to this characteristic highly influence the permeability of the membrane. Figure 4 shows the porosity properties of PSf/PANI at different concentration of PANI. From the graph, it is clearly shows that membrane porosity increased as PANI concentration increases up to 10 g PANI (sample 3). The increased of membrane porosity might be due to the increased of membrane pore as PANI introduced in dope solution. This result is in line with SEM result which shows that the size of membrane finger-like structure increased as PANI concentration increases. The similar results were found by Zhu et al. (2015) where the porosity increased as the content of PANI increases.

However, as PANI concentrations increases up to 15 g, the porosity of membrane tend to decreased. This result might be due to membrane pore was blocked by PANI. Although the presence of PANI increases the membrane pore size, the excess amount PANI will densified the membrane and will filled the membrane pore. Thus, membrane porosity reduces.

The mean pore sizes represent the average size of membrane pore on the surface of membrane. Figure-6 shows the effect of PANI on membrane pore size of PSf. As shown in the figure, the membrane mean pore size increased with 5 wt.% of PANI content. This result might be due to pore size enlargement in membrane as proven by porosity result. However the mean pore sizes tend to decreased with addition of 10 and 15 g PANI. This result might be due to the presence of PANI on membrane surface which reduce the mean pore size of membrane. The reduction of pore size is important to improve membrane rejection properties.

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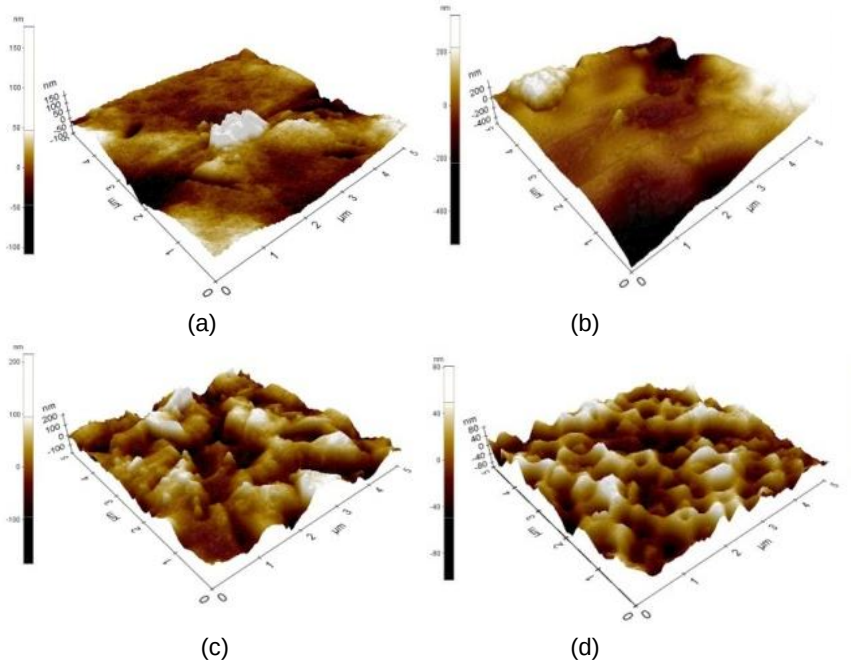


*Figure 3: Surface roughness of PSf membrane at different loading of PANI, (a) 0 wt. % PANI ($R_a$: 12.64 nm), (b) 5 wt. % PANI ($R_a$: 20.43 nm), (c) 10 wt. % PANI ($R_a$: 38.42 nm), (d) 15 wt. % PANI ($R_a$: 80.24 nm)*

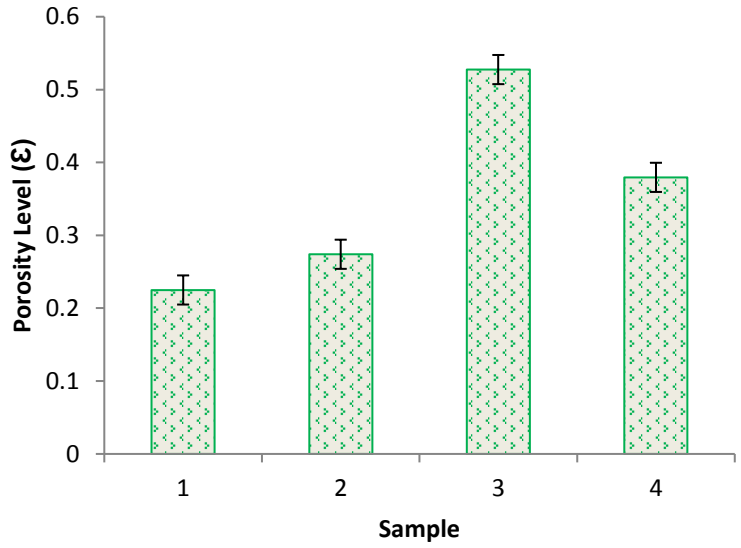


*Figure 4: The porosity level of the membrane*

## 4. Conclusions

In this study, the modification of PSf membranes containing different concentration of Polyaniline (PANI) as an additive was successfully prepared using polymer blending method. Difference concentration of PANI does affect the properties of the membrane surface. The characterization of the membrane had been observed via Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Atomic Force Microscopy (AFM) and porosity test. The result showed that PANI concentration had highly influenced the membrane properties and performance. FTIR result proved that the PANI was capable to reduce membrane hydrophilicity by contribute amine group which is polar structure. SEM result showed that PANI did enhance the membrane porosity. Membrane surface roughness was also found to be increased with addition of PANI. From this study, the result suggested that PANI is suitable to be an additive in membrane fabrication.

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