

Characterization of Polydopamine-Coated Polyethersulfone (PES) membrane for water purification

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Abstract. The polyethersulfone (PES) membrane has been prepared by phase inversion method using N-methyl-2-pyrrolidone (NMP) as solvent and polydopamine (PDA) as additive. The fabricated membrane was modified by coating with PDA of 0.5 g/l concentration and 180 minutes immersion time. The characteristic of the PES membranes before and after the modification was studied in this paper. The result of the pure water permeation experiment showed that the PDA-coated PES membrane showcased a higher flux than that of pure PES membrane. Scanning Electron Microscopy (SEM) analysis confirmed that the membrane had an asymmetric structure consisting of two layers. There was no significant influence on the addition of PDA to the morphology of the pore matrix because the modification was done by surface coating. Fourier Transform Infrared Spectroscopy (FTIR) analysis showed that PDA was successfully introduced on the surface of PES membrane with the appearance of peak O-H from catechol at wavenumber of 3348 cm⁻¹. Modification with PDA increased the mechanical strength of the membrane which affirmed by the results of the tensile and elongation at break evaluation.

1. Introduction

The shortage of clean water continues to increase and has become a pivotal issue. Water sources such as rivers, lakes and ground water have been contaminated directly or indirectly by industrial waste disposal [1, 2]. Many approaches have been done to remove humic acid contained in water, such as by coagulation method [3], flotation [4, 5], plasma [6], magnetic carbon [7] and ultrafiltration membranes [8].

Membrane technology is one of the most effective and widely applied methods for water purification process. Membranes have been widely used in the food industry, pharmaceutical, biotechnology, water treatment and other fields due to their excellent performance, low energy consumption, good selectivity, no phase change and operation can be done at room temperature [9]. Ultrafiltration process is generally employed for water purification process because this process has proven effectively in removing organic macromolecules in water [8, 10, 11]. Polyethersulfone (PES) is one of the most commonly applied membrane in membrane separation due to its outstanding chemical resistance, as well as thermal and mechanical stability [12]. However, fouling on the membrane is a major constraint in the application of this process [13], especially on hydrophobic



polymer based like PES. Fouling has a negative effect on membrane performance by decreasing the flux value, membrane selectivity, and also increasing the operating cost [13].

In order to reduce the occurrence of fouling, modification is done to the membrane by adding another substrate be it inside or on the surface of the membrane [14, 15]. Coating is a very simple and most used technique to modify the membrane surface. Surface coating using polydopamine has been really popular nowadays [15-17]. PDA attracted the attention of many researchers because of its adhesiveness to any substrate [18]. In addition, PDA coating can reduce the hydrophobicity of membrane due to its superhydrophilic nature [19]. More hydrophilic surface of membrane improves the antifouling as well as enhancing the membrane performance in terms of flux and selectivity.

However, modifications must be designed in such a way as to obtain the right conditions. Excessive addition of additive will also negatively impact the characteristics and performance of the membrane. Such as that reported by [20], long immersion time in a dopamine solution caused the coating layer to become thicker on the membrane surface which leading to pore blockage and resulted in the decrease of flux of the membrane. Similar case was also proposed by [21] on the concentration of PDA.

In this present study, the research team has been working on observing the ideal condition for PDA coating by varying concentrations and immersion times. However, in this paper, only the characterization results of the modification experiment performed using polydopamine at a concentration of 0.5 g/l with immersion technique for 180 min will be discussed. The base membrane used is Polyethersulfone (PES) prepared using phase inversion method. Membranes were characterized by conducting pure water permeability tests, functional group tests, membrane morphological structure tests and tensile tests.

2. Experimental

2.1. Materials

Polyethersulfone (PES) was used as the main polymer. N-methyl pyrrolidone (NMP) was utilized as a solvent and aquadest as a non-solvent. Dopamine hydrochloride and tris-HCl buffer with pH 8.8 was used to make polydopamine (PDA) solution to coat the membrane surface. UV-VIS 1700 Shimadzu Spectrophotometer, Scanning Electron Microscopy (SEM), and Fourier Transform InfraRed (FTIR) Shimadzu 8400 and a dead-end ultrafiltration module were used to characterized the prepared membranes.

2.2. Preparation and Modification of PES Membrane

Polyethersulfone (PES) of 17.5 wt% was dissolved into 82.5 wt% NMP solvent. This mixture was stirred using a magnetic stirrer until homogeneous. The result of this stirring is called Dope PES. Dope was then stored into the freezer to remove air bubbles that are still present in the solution. Dope was removed from the freezer and allowed to reach room temperature. Dope was then casted by pouring it on a glass plate (casting process) and flattened onto the entire surface of the glass plate. The casted film on the glass plate was afterward immersed in a coagulation bath containing the aquadest that serves as a non-solvent (precipitation process). The formed membrane was then stored in a container containing aquadest.

Membrane modification was done by dissolving dopamine hydrochloride into 15-ml tris-HCL buffer solution (pH 8.8). Following that, the solution turned into a brownish color indicating the formation of polydopamine solution. The fabricated UF PES membrane was then immersed in 0.5 g/l polydopamine (PDA) solution for 180 minutes. The membranes were denoted as M1 for Pure PES and M2 for PES immersed in PDA for 180 minutes.

2.3 Membrane Characterization

The characterization of membranes was carried out in terms of pure water permeability, membrane morphology, functional group, and tensile test. Determination of pure water flux was done by dead-end filtration flow method. The test was performed by means of an ultrafiltration module. Aquadest was passed through the module and the pressure was given (1, 1.5, 2, 2.5 and 3 bar) to produce permeate. The permeate was collected and measured every five minutes.

The structural morphology of the membranes was analyzed using Scanning Elctron Microscopy (SEM). The SEM test aims to determine the surface structure and pore size of the membrane. The sample was dried prior analysis, then immersed in liquid nitrogen for a few seconds until it solidifies and the membrane was then broken. The specimen was then placed on a sample holder and its structure was observed. Membrane functional groups were investigated using the Fourier Transform InfraRed Spectroscopy (FTIR) instrument. Type of equipment used was FTIR Shimadzu 8400. Membrane samples were analysed at wavelength 500 cm^{-1} - 4000 cm^{-1} . The mechanical properties evaluation was conducted in Laboratory of Physics, Syiah Kuala University, Banda Aceh, Indonesia. Specimens of membrane were stretched to the breaking point, and in doing so, the tensile strength and elongation were determined.

3. Results and Discussion

3.1. Pure Water Flux (J_w)

Flux is the volume of permeates that passes through each unit of membrane area in a given time. Figure 1 shows the value of pure water flux on pure PES membrane and PES/PDA membrane. The pure water flux of PDA-coated membrane is greater than that of pure PES membrane. In the unmodified membrane (M1), the fluxes obtained at the operating pressures of 1, 1.5, 2, 2.5 and 3 are 10.15, 23.6, 29, 41.7, and 48 $\text{L/m}^2\cdot\text{hour}$. Whereas on the membrane after modification, the pure water fluxes obtained at the same operating pressure are slightly higher which are 15.5, 24.9, 35, 45.5, and 55.6 $\text{L/m}^2\cdot\text{hour}$, respectively. An increase in the flux of pure water is due to increased hydrophilicity of the membrane with the addition of PDA as additive. Hydrophilic membranes tend to pass through the membrane pores as opposed to hydrophobic membranes [22]. Thus, water diffuses faster which confirms the enhance of pure water flux.

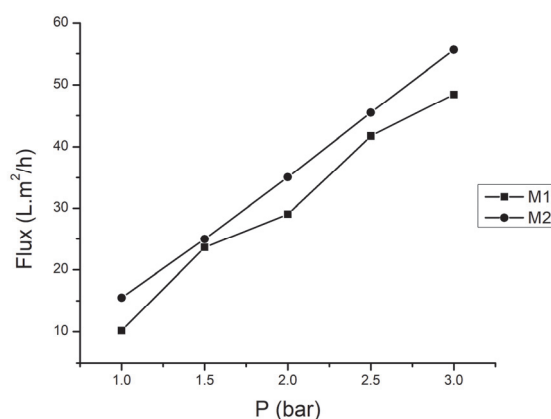


Figure 1. Pure water flux of M1 and M2 membranes at each operating pressure.

3.2. Membrane Morphology

The results of surface and cross-sectional structure of the membrane observed using Scanning Electron Microscopy (SEM) with 10 kV voltage can be seen in Figure 2. PES/PDA membrane surface structure is seen denser and has smaller pore size than that of pure PES membrane. This result is in accordance with the research done by [23] which reported that the addition of PDA can decrease the pore size of

the membrane. In addition, PDA coating can cause the membrane surface to become rough. This can occur due to the formation of PDA nanoaggregates on membrane surfaces [24].

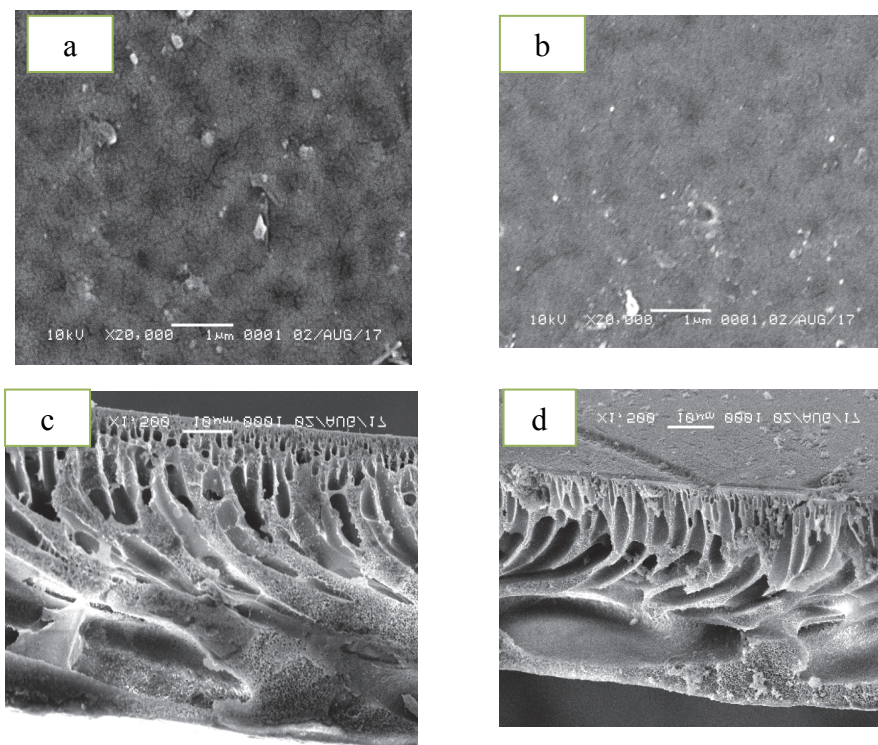


Figure 2. SEM imaging of (a) surface structure of uncoated PES membrane, (b) surface structure of PDA-coated PES membrane, (c) Cross sectional structure of uncoated PES membrane, and (d) Cross-sectional structure of PDA-coated PES membrane

The SEM observation results of cross sectional structures on both membranes evidencing that the prepared membrane has an asymmetrical structure with two layers, where the top layer is thinner with tight pores, while the lower layer has a larger pore size which serves as a support and provides resistance to membrane. The upper layer of the PES/PDA membrane has a greater thickness than the pure PES membrane. There is no noticeable change in the matrix portion of the membrane after modification. This is because the modification was done by coating on the surface. Therefore, only membrane surface is affected.

3.3. Functional Groups Analysis

The investigation of functional groups presence on the membrane was analyzed by FTIR device, and the result is shown in Figure 2. Regarding to Fig. 2, in M2 membrane, there is a new peak appearance at spectrum range of $3300\text{--}3700\text{ cm}^{-1}$. This peak is confirmed to be O-H and N-H bands of catechol group from PDA [25]. This can be taken as indication that PDA has successfully been deposited on the membrane surface. However, another specific indolequinone peak should be emerging on the 1700 cm^{-1} wavenumber [26]. However, it is not detected in the analysis, could be due to the low of concentration and length of immersion time.

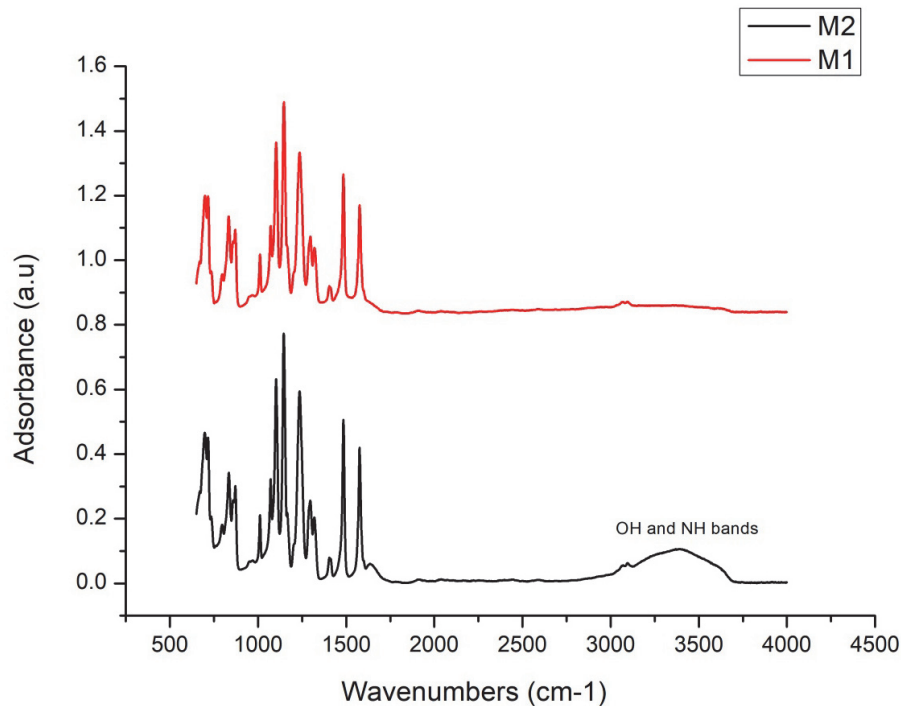


Figure 3. Chemical composition of PES membrane with (M2) and without (M1) PDA-coating as observed by FTIR

3.4. Mechanical Properties

Table 1 shows the results of mechanical strength measurement of membranes before and after modification. Mechanical strength tested is tensile strength and elongation at break. From the results, it can be observed that both tensile and elongation at break improved in the membrane after coating with polydopamine. Pure PES membrane had tensile value of 11.80 kgf/mm² and elongation at break of 36.62%. While on the membrane coated with polydopamine with concentration of 0.5 g/l for 180 minutes, tensile strength and elongation at break reached up to 19.30 kgf/mm² and 73.50%, respectively. This is because the PDA particles reduce the fragility of the membrane through the occurrence of energy absorption during tensile deformation [27]. High tensile strength and elongation means the membrane is not brittle or more ductile and not easily broken or damaged despite given a heavier workload. These characteristics have an effect on the length of membrane life-time

Table 1. Mechanical properties of pure and modified PES membranes

Membrane	Tensile Strength (kgf/mm ²)	Elongation at break (%)
M1	11.80	36.62
M2	19.30	73.50

4. Conclusions

Polyethersulfone (PES) ultrafiltration membrane has been prepared and modified using 0.5 g/l polydopamine by dip-coating for 180 minutes. The aim was to improve the antifouling of the PES membrane by enhancing the hydrophilicity. The effect of modification on the PES membrane was observed through a pure water flux test, composition analysis using FTIR, morphological test by means of SEM and mechanical strength. Based on the result of characterization it can be concluded that polydopamine has been successfully coated on membrane surface which confirmed by the appearance of N-H and O-H peak from catechol at wavenumber of 3348 cm⁻¹. PDA coating result in a narrowing of the pore on the membrane surface. The presence of PDA has an effect on the increase of

pure water permeation due to the hydrophilic nature of the PDA. In addition, the PDA also improved the mechanical properties of the membranes in terms of tensile and elongation at break.

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