The Effects of Solvent Type on The Performance of Flat Sheet Polyethersulfone/Brij58 Membranes

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Abstract. Selection of the appropriate solvent plays an important role in the characteristics of the membrane formation. Flat-sheet polyethersulfone (PES) membranes were formation via non-solvents induced phase separation (NIPS) technique. PES as a polymer, Brij58 as hydrophilic surfactant and three types of solvent were used to prepare the dope solution. This paper attempts to show the effects of three different solvents there are; dimethylsulfoxide (DMSO), dimethylformamide (DMF), and dimethylacetamide (DMAc) on characterizations and performance of fabricated membranes. The fabricated membranes in this study were characterized by measuring water contact angle and mechanical properties. The performance of fabricated membranes was carried out using a dead-end ultrafiltration module. Solubility between solvent and non-solvent is an essential factor in the membrane formation process. The porosity of membrane fabricated from the system of PES/Brij/DMAc was higher than membrane made from another system, so that the water permeability of this membrane was higher than others. The membrane fabricated with DMAc as solvent had a tensile strength of 12.42 kgf/mm².

1. Introduction
In recent years, membrane separation processes compete with conventional separation processes in many applications. However, membrane separation processes have several advantages such as no use of chemicals, and energy consumption is relatively low, the process is simple, easy to be integrated with other methods, as well as secure in operation. Membrane separation processes have been applied to a variety of processes, including water purification [1], in the food and medicine industries [2], and on industrial waste treatment processes [3]. Since the invention of the phase inversion method, a large number of researchers have studied the mechanism of membrane formation. In order to produce asymmetric membranes, phase inversion process is a straightforward technique that is commonly used [4]. In the membrane separation process, the newly cast membrane is immersed in a non-solvent bath (a compound having a high affinity for the solvent and a low affinity for the polymer). Then the precipitation begins to occur because of the solubility of the polymer, and the non-solvent is low. At the same time, a high solubility between the solvent and non-solvent causes the diffusion process occurs at some point solvent change with non-solvent) which causes demixing. The sublayer formation
of the asymmetric membrane was controlled by several variables in the casting solution such as composition, coagulation temperature, organic and inorganic additives [5]. Also, the formation of asymmetric membranes was also influenced by the polymers, solvents, and non-solvents used [6].

Several parameters have been investigated concerning the mechanism of membrane formation on morphology and membrane performance for membrane separation processes such as the effect of polymer concentration in casting solution [7], type of solvent and non-solvent used [8], the addition of additives [9] [10].

These parameters influence the process of instantaneous/delayed demixing that occurs in the coagulation bath. Polyethersulfone (PES) is one of the polymers that commonly used as the main polymer to fabricate ultrafiltration membranes. Besides having a high temperature resistance, wide pH tolerance, PES also have good mechanical strength and are also easy to produce [11].

In this study, the PES membrane was prepared by phase inversion technique with several solvents. The solvents used were dimethylsulfoxide (DMSO), dimethylformamide (DMF), and dimethylacetamide (DMAc). The characteristics of fabricated membranes were characterized in term of morphology, hydrophilicity, and mechanical properties and also the ultrafiltration performance.

2. Methods

2.1 Materials
The primary material of the membranes was Polyethersulfone (PES, Ultrason E6020 P). Three types of solvents used were dimethylsulfoxide (DMSO, Wako Pure Chemical Industries, Japan), dimethylformamide (DMF, Wako Pure Chemical Industries, Japan), and dimethylacetamide (DMAc, Wako Pure Chemical Industries, Japan). Deionized water as non-solvent, Brij58 (Mw 1,124) (Sigma Aldrich Co., LLC, Germany) as an additive, and humic acid solution (Sigma Aldrich Co., LLC, Germany) was used as the artificial sample for water contamination.

2.2 Membrane preparation
An 18 wt% of PES and 7 wt% of Brij58 was dissolved in DMF, DMAc, and DMSO, respectively. Membranes are made in phase inversion by a nonsolvents induced phase separation (NIPS) technique. The casting knife with a set thickness of 2 mm was used to cast the polymer solution onto the glass plate. The precipitation process of the membrane was done in the non-solvent bath containing deionized water.

2.3 Characterization of membrane
The morphology, and the hydrophilicity of membrane surface were characterized using Field Emission Scanning Electron Microscopy (FE-SEM, JSF_7500F, JEOL Co. Ltd, Japan), and water contact angle (Drop Master 300, Kyowa Interface Science Co., Japan), respectively. The mechanical properties of membrane was checked using a tensile test instrument (Autograph AGS-J, Shimadzu Co., Japan).

2.4 Water flux
A dead-end filtration module was used to study the filtration performance of fabricated membranes. Water was then carefully filtered through the membrane with operating pressure
of 1 bar. The weight of water permeate was measured every 5 minutes. Afterward, Equation (1) was used to calculate the flux of pure water [4]:

\[ J = \frac{\Delta V}{A \times \Delta t} \]  

(1)

where \( J \) is Flux (l/m^2.h), \( V \) is permeated volume (L), \( A \) is the effective membrane area (m^2) and \( t \) is the permeation time for DI water (h).

3. Result and Discussion

3.1 Membrane Morphology

Figure 1 shows an overview of the top surface of fabricated membranes, which were fabricated from the system of PES/Brij/DMF, PES/Brij/DMAc, and PES/Brij/DMSO. The formation of pores on membrane is influenced by the thermodynamic and kinetic parameters of the dope solution. The process is initiated by the evaporation of solvent to form an active top layer. Furthermore, the membrane condition can be considered stable where the solvent and non-solvent diffuse in the coagulation bath [12]. The formation of sublayer is highly impacted by the rate of diffusion in the non-solvent bath. If there is an instantaneous demixing process, the solvent diffusion to the coagulation bath will be slow, as well as to the non-solvent diffusion into the membrane. This will result in a larger pore size than the delayed demixing [13].

Solubility between solvents and non-solvents is one of the influential factors in the membrane making process. Non-solvent with lower difference of solubility to solvent diffuses more easily into the polymer film which causes an increase in the diffusion rate between the solvent in the polymer film with the non-solvent in the coagulation bath which causes spontaneous separation. The separation can normally be seen from the formation of pores on the membrane surface [14].

Solubility data of non-solvent (i.e. water) and all solvents (i.e. DMAc, DMF, DMSO) used in this study is presented in Table 1. It is shown that, amongst all the solvents, DMAc has the closest solubility value (smallest difference) to water, whereas DMSO has the biggest difference. These data support the idea of why using DMAc as a solvent produced membrane with better porosity property in comparison to those using DMF and DMSO.
Table 1. Solubility parameter

| Solvent/non-solvent | \([\text{J/cm}^3]^{0.5} \times 10^{-3}\) |
|---------------------|------------------------------------------|
| DMAc (s)            | 22.1 [14]                                |
| DMF (s)             | 24.8 [14]                                |
| DMSO (s)            | 26.6 [15]                                |
| Water (ns)          | 19.2 [14]                                |

3.2 Water contact angle measurement

Membrane performance such as permeation and antifouling properties is related to the hydrophilic or hydrophobic property of the material, which can be evaluated by using water contact angle meter. The membrane with smaller contact angle values has higher hydrophilicity. The results obtained from the water contact angle analysis of membranes fabricated using different solvents are presented in Figure 2. The order of the contact angles for the resulting membrane are DMAc > DMF > DMSO, it means that the membrane prepared with DMSO has the lowest water contact angle but highest hydrophilicity. Otherwise, the membrane prepared with DMAc present highest water contact angle and in other words, this membrane more hydrophobic than others.

![Figure 2. Water contact angle of fabricated membrane](image)

In addition to solvent influence, water contact angle is also influenced by the addition of hydrophilic surfactant (Brij58) in dope solution. Effects of surfactant additive on membrane properties were studied in previous research [10].

3.3 Mechanical Property

Mechanical properties of all the membranes which prepared using different solvents were measured and results are presented in Table 2. It is seen that both tensile and elongation at break of PES membrane shows a declining trend with DMAc>DMF>DMSO order. As presented in Table 2, the membrane established with DMAc as solvent had the highest tensile strength of 12.42 kgf/mm². The membrane fabricated with DMF and DMSO as a solvent followed with tensile strength values of 10.89 kgf/mm² and 8.32 kgf/mm², respectively. A possible
explanation for these results may be related to the thickness reduction of the surface layer due
to the acceleration of diffusion during the precipitation process in non-solvent bath.

Table 2. Mechanical properties of the fabricated membranes

| Membrane     | Tensile strength (kgf/mm²) | Elongation at break (%) |
|--------------|----------------------------|-------------------------|
| PES/DMAc     | 12.42                      | 56.66                   |
| PES/DMF      | 10.89                      | 56.10                   |
| PES/DMSO     | 8.32                       | 45.94                   |

Table 2 also presents the obtained values of elongation at break. The elongation at break of PES/DMAc, PES/DMF, and PES/DMSO membranes were 56.66, 56.10, and 45.94%, respectively. These results suggest that, all the membranes fabricated in a DMAc system is more elastic in comparison to those using DMF and DMSO.

3.4 Filtration Test

Filtration test is performed to determine the amount of flux. The water flux can be evaluated on the basis of the amount of generated permeate during filtration. Water filtration is performed by using distilled water at constant pressure (1 bar) and the permeate volume was measured every 5 minutes. In the membrane filtration process, generally, the water flux decreases until the condition is constant. The decrease in water flux is not caused by an impurity (foulant), but due to the possibility of compacting pressure partially closing the pores. This is because the pore structure is not uniform so that the direction of the flow leads to changes in the pore structure to a certain shape and the flux is said to be constant [16].

For the application in water treatment, pure water flux is an important characteristic that should be possessed by a membrane. Figure 3 shows the membranes porosity as well as their fluxes from filtration experiment using pure water as feed. The results in Figure 3 show a correlation between flux of pure water and porosity of the membranes in which both show similar declining trend with orderly manner of DMAc>DMF>DMSO. The membrane prepared in PES/Brij/DMAc system showcased the highest PWF amongst the other solvent systems. The reason is because using DMAc solvent resulted in membrane with higher porosity. The PES/Brij/DMAc membrane produced a PWF of 21.308 with porosity of 9%. Meanwhile, PES/DMSO has the lowest PWF which consistent to its lower porosity, which was 8.2517 L/m².h.

It is obvious that there is a direct correlation between the pure water flux and porosity. Highly porosity of membranes produced higher pure water flux. While membranes with low porosity produced lower pure water flux. The selection of solvents plays a vital role in the porosity and PWF of all membranes tested. If the difference in solubility is small, the resulting membrane has a higher porosity. Membranes with a dense top layer are formed when the difference in solubility is high [17].
4. Conclusion
This study set out to investigate the effect of solvent type on the characterization and performance of PES/Brij58 membranes. This study has identified the effects of three type of solvents (DMAc, DMF, DMSO) on the membrane porosity, mechanical properties, and pure water flux. The results of this experiments show that the selection of solvents plays a vital role in the PWF of all membranes formed. Fabricated membranes using DMAc as a solvent has higher porosity than membranes fabricated using DMF and DMSO as solvents so that the resulting pure water permeability higher than other membranes. Solubility between solvent and non-solvent is an important factor in the membrane formation process.

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