Morphology and filtration performances of polyether sulfone membrane modified with carbon and Fe$_2$O$_3$

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Abstract. Membrane separation technology has been widely applied in various industrial sectors. Some modification on membrane composition and structure is conducted to improve membrane filtration performance and mitigate fouling phenomena. Fouling on membrane surfaces lead to decrease permeability, increase energy consumption, and shorten membrane life time. The aim of this study is to manufacture PES membrane which involved inorganic additives consists of Carbon and Fe$_2$O$_3$ particles to mitigate fouling tendency. All of membranes were prepared using phase inversion method with dissolving PES polymer into dimethyl formamide (DMF). The result membranes were characterized using Scanning Electron Microscopy (SEM) to investigate morphological structure and breaking strength to determine mechanical property. Membrane filtration performance were tested using soy protein solution in cross-flow system. The results showed that the addition of inorganic particles in PES membrane caused the increasing of pores which lead to increase pure water flux from 15.14 L/m$^2$.h to 58.67 L/m$^2$.h. Fouling mitigation test towards soy protein also showed that carbon and Fe$_2$O$_3$ particles enhanced membrane flux recovery ratio from 64.5 to 76%. Furthermore, the inorganic particles presence in PES membrane also improved the tensile strength of membrane up to 128 Mpa.

1. Introduction

Polymer-based membranes are commonly used in the separation industry because it requires lower energy for operation and maintenance. The membrane can be formed from a polymer, inorganic materials, or the combination of organic and inorganic chemicals. One of the polymers used as a membrane material is polyethersulfone (PES). PES contains ether and sulfone chains which alternate between benzene rings to provide a unique structure with high mechanical, and resistance to extreme liquids [1-3]. Conversely, the hydrophobic nature of PES is the drawback of its application in ultrafiltration for purification of water or concentrated of protein. Flux declined is easily occur on membrane filtration due to fouling phenomena. 

Many researchers modify the membrane structure to maintain the stability of filtration. Several inorganic substances have been used, such as Al$_2$O$_3$, SiO$_2$, ZnO, TiO$_2$. Uzal et al [4] produced
membranes via non-solvent induced phase separation technique by blending Al2O3. The membranes with increased mechanical strength, higher porosity, large flux rates, and lower water contact angle were successfully obtained. Other authors used Fe2O3 as an additive to produce polyvinyl chloride membrane. It is confirmed that the addition of Fe2O3 nanoparticles greatly enhances the overall pore structure of the membrane. The hydrophilicity properties of the membrane were also increased. The addition of Fe2O3 into polymer solution may increase the mechanical strength, water permeability, and antifouling performance [5].

In this research, nanocarbon obtained from palm kernel shells and Fe2O3 synthesised from local minerals are tried to modify the PES membrane. The addition of carbon in the membrane solution is expected to increase the pore size of the membrane, and the addition of Fe2O3 is expected through physical mixture will result in increased membrane hydrophilic properties. The aim of this study is to analyze the effect of those additive on the morphology and filtration performance of blended PES membrane. The performance of membrane filtration for soy protein concentrate is also discussed.

2. Materials and Methods

2.1 Materials

PES with an average molecular weight of 65,000 Da (BASF, Ludwigshafen, Germany) was used as the main polymer to prepare flat sheet membrane. Dimethyl formamide purchased from Merck KgaA, Germany was supply as solvent to dissolve the polymer. Fe2O3 and nanocarbon was kindly provided by Physic Science Laboratory and Energy laboratory of Syiah Kuala University, respectively.

2.2 Membrane Preparation

For original membrane, the dope solution is prepared by mixing 16wt% of PES in DMF. In other dope solution, nanocarbon and Fe2O3 of 0.05wt% was added separately to prepare the modified PES membrane. The detail composition of membrane solution are summarized in Table 1. All dope sample is stirred for about 24 hours to obtain the homogeneous solution. After releasing air bubble, the solution is poured onto a glass plate using an applicator knife with a thickness of 300 μm. The casted solution and the glass plate then dipped in a coagulation bath containing pure water for solidification of membrane.

| Sample | Composition (wt%) |
|--------|------------------|
|        | PES  | DMF  | Fe2O3 | Carbon |
| M1     | 16   | 84   | -     | -      |
| M2     | 16   | 83.95| 0.05  | -      |
| M3     | 16   | 83.95| -     | 0.05   |

2.3 Membrane characterization

The cross-section structure of the membrane is visualized using Scanning Electron Microscopy (SEM, JSM-7500F, JEOL Ltd., Tokyo, Japan). A standard sample preparation procedure was provided consist of drying in a freeze dryer, immersing in liquid nitrogen for membrane fracture, and coating with osmium for sample imaging.

In order to analyze mechanical property of original and modified PES membrane, a tensile strength measurements was carried out by using a Universal Testing Machine (Autograph AGS-J, Shimadzu Co. Japan). A membrane samples were cut into pieces of 5 cm length and at least 2 tests for each type of the membranes were made and the average was reported in this paper for the tensile strength.
2.4 Filtration performance

Filtration performance of the fabricated membrane was analyzed in term of water flux and flux recovery ratio (FRR). Pure water flux is calculated from the volume of water that passes through the effective surface area of the membrane during filtration period. Filtration experiment was carried out at constant pressure (1 bar) on the cross-flow module and the permeate is taken every 10 minutes.

Moreover, a 5000 ppm soy protein solution was also filtrated using the same module to investigate the FRR profile of the membrane. Flux of membrane during filtration of water was calculated using Equation (1).

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

Where:

- \( J \) = Flux (L/m\(^2\).hour)
- \( V \) = permeate volume (L)
- \( A \) = membrane surface area (m\(^2\))
- \( t \) = Time (hour)

3. Result and Discussion

3.1 Membrane Structure

Scanning Electron Microscopy (SEM) is an instrument used in observing the morphology of membranes. Membrane morphology is one of the crucial parameter for manufacturer in determination of the specific application in the separation industry. In this study, the imaging of SEM was taken only on the cross-section part of the membrane. Fig. 1 shows the cross-sectional structure of the resulted membranes with magnification of 2000X.

![SEM image of membrane morphological structures](image1)

**Figure 1.** SEM image of membrane morphological structures
The modified membrane with addition of Fe$_2$O$_3$ (M2) possesses longer fingerlike pores than the pristine membrane (M1), while the presence of carbon particles in membrane solution lead the increasing number of finger pores [6].

3.2 Mechanical Properties of Membranes

Tensile strength of membrane is an important parameter to determine the mechanical property of membrane. Membrane with a denser structure commonly has better breaking strength than the porous membrane [6]. Tensile strength of prepared membranes are presented in Fig. 2.

![Graph showing tensile strength of prepared membranes](image)

**Figure 2.** Tensile strength of prepared membranes

Fig. 2 showed the increasing of PES membrane breaking strength after modification with Fe$_2$O$_3$ and carbon particles. The PES membrane with the addition of 0.05% carbon (M3) showed the strongest tensile strength with 128.56 MPa compared to PES/Fe$_2$O$_3$ (M2) and PES (M1) membrane with 114.5 Mpa and 102.626 MPa, respectively. It is due to the adhesion forces between carbon particles and PES polymer that lead the increasing of membrane tensile strength [7]. Moreover, the presence of Fe$_2$O$_3$ particles scattered in membrane solution can limit the movement of polymer chains leading to the improvement of membrane mechanical strength. The same result was reported by Ng, et al [8].

3.3 Filtration Performance

Fig. 3 showed the pure water flux of all membranes conducting in cross-flow filtration system. The pure water flux of PES membrane increased from 15.14 L/m$^2$.h to 51.98 and 58.67 L/m$^2$.h after addition of Fe$_2$O$_3$ and carbon additives, respectively. The presence of the hydroxyl and oxygen group in the particles increase the hydrophilicity of PES membrane solution and has strong interaction with water in coagulation bath [9]. As a consequence, the exchange rate between solvent and non-solvent during precipitation increased, leading the formation more porous structures (as shown in Fig 1). It is well-known that more porous structure in membrane produced higher permeation.
The filtration of soy protein was also carried out using a cross-flow filtration module for 60 minutes recirculation process. A 5000 ppm soy protein solution was pumped to the module at filtration pressure of 1.0 bar. The concentration of soy protein in permeate and retentate tank was analyzed by using spectrophotometer UV-Vis. It is found that, the rejection of soy protein filtrated with M2, and M3 membrane was 30.40 and 40.50 %, lower than the original PES membrane (M1) which is rejected about 50%. However, the filtration duration of M2, and M3 was better than the M1 membrane. The presence of inorganic additive in membrane surface brought about the reducing the interaction between protein and membrane surface leading to easier passes of water through the membrane [11-12].

4. Conclusions
Modification of PES membrane has been successfully fabricated by blending of nanocarbon and \( \text{Fe}_2\text{O}_3 \) into the polymer solution. PES/carbon membrane exhibited more porous and highest pure water flux of 58 L/m\(^2\).h. The addition of \( \text{Fe}_2\text{O}_3 \) particles improved membrane mechanical properties. Filtration of soy protein was better employed by modified membranes.

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