Preparation and Characterization of Fly Ash Additive-Modified Polyether-Based Membrane

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Abstract

Recently, Polyethersulfone (PES) polymer material based on flat sheet membranes reached much attention in membrane technology. However, PES polymer has low hydrophilicity. This study describes PES-based membranes incorporating fly ash as an additive. The first analysis was conducted by Fourier Transform Infrared, Scanning Electron Microscope, tensile strength, and porosity tests. Four membranes, including pure PES membranes, were prepared via the phase inversion process, namely MA–0, MA–0.1, MA–1, and MS–1. The characteristics of the membrane samples were analyzed in terms of chemical group, morphology, mechanical and membrane surface hydrophilicity. The characterization results show that additive incorporation increased pure water flux performance, and the highest pure water permeability increased up to 70% by the MA–1 membrane. Moreover, it increased by 19% compared to pure silica-modified PES membrane (MS–1). In addition, the MA–1 membrane at a pressure of 3 bar reached significant performance in the trend of pure water flux values because of these improvements in membrane characteristics. The membrane also shows a higher tensile strength with adding additives to the membrane prepared.

Keywords: chemical group, fly ash, membrane, morphology, permeability

1. Introduction

Polyethersulfone (PES) is a commonly utilized separation membrane material. Because of its outstanding chemical and physical qualities are particularly resistant to very low pH and has good mechanical properties (Shen et al., 2012). However, because of PES hydrophobicity, membranes are quickly fouled, resulting in decreased flux during membrane performance (Zhao et al., 2013). Various approaches have been explored to obtain high-capacity PES membranes. One is that by adding hydrophilic additives to the membrane, an impression solution is one approach to improve its properties (Aprilia, 2018; Mulyati et al., 2020).

Fly ash (coal fly ash) is a smooth, spherical, pozzolanic waste product from coal combustion in a steam power plant furnace (Darmayanti et al., 2019). Fly ash is a fine-grained gray-colored particle that is produced by the burning of organic molecules. Fly ash is made up of chemical elements, such as silica (SiO₂), alumina (Al₂O₃), ferrous oxide (Fe₂O₃), and calcium oxide (CaO). Fly ash is one of the alternatives that can be used as a base material because of the presence of high silica content. The addition of fly ash can improve the membrane’s permeability and selectivity by increasing pore dispersion (Diana et al., 2018). Cheng et al. reported the use of fly ash-based ceramic membrane with maximum recovered flux reached 5.22 kg/(m²-h)(Cheng et al., 2020). In this case, using fly ash as a material, the current work suggests fabricating a flat sheet PES-based membrane at a lower cost (Zulkifli et al., 2019).

Nanocomposite membranes, as a new category of membrane materials, composed of inorganic nanomaterials and organic polymers have attracted a wide field of research for water treatment. This type of membrane can provide impressive nanomaterial characteristics due to its large surface area volume proportion into the targeted application. Various inorganic nanostructures have been used for this purpose, including; silver (Ag), titanium (TiO₂), silicon (SiO₂), aluminum (Al₂O₃), iron (Fe₃O₄), zinc (ZnO) and zirconium (ZrO₂) nanoparticles (Al-Araji et al., 2021).

The incorporation of metal oxide nanomaterials into polymers not only harmonizes the structure and physicochemical properties, such as hydrophilicity, porosity, charge density, and chemical, thermal, and mechanical stability of membranes, but also introduces unique functions such as...
antifouling and photocatalytic characteristics into the membrane (Tewary, 2018). If the interaction is weak between the nanoparticles and the polymer chain, there is a possibility that the nanoparticles will be released from the membrane structure (Mannan et al., 2022). If this were to occur, it would result in reduced overall membrane performance as environmental concerns increased and concerns about the fate of the membrane in the final stream. Fly et al., 2018, have studied the effect of nanoclay on PVDF membranes, other types of nanofillers have shown increased flux, fouling resistance, mechanical strength and abrasion resistance with proper choice of filler and loading. However, only a few studies have done so considered as nanoparticles in the presence of additives such as PEG or PVP which can act negligibly influence of nanoparticles on surface properties.

The purpose of this study is to evaluate the performance of membranes modified with fly ash additives. Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), tensile strength, and porosity will all be used to characterize each manufactured membrane. Furthermore, pure water flux is included in the membrane performance.

## 2. Methodology

### 2.1. Materials

The primary membrane polymer used was polyethersulfone (PES, BASF Ultrason E6020, Germany), with solvent of dimethylacetamide (DMAc, Merck, Germany), and fly ash as membrane additives. Fly ash was obtained from the Nagan Raya power plant in Aceh Province, Indonesia.

### 2.2. Membrane Preparation

A total of four flat-sheet membranes were fabricated in this study using the Nonsolvent-induced phase separation (NIPS) technique. The composition of the membrane was presented in Table 1. The membrane was manufactured by dissolving PES and fly ash with DMAc solvent in a glass bottle for 24 h with magnetic stirrer at room temperature. This mixed solution was referred to as a dope solution, which was then left at room temperature for 4 h to remove air bubbles. The next step was membrane casting, which involved pouring the dope solution onto a glass plate and molding it with casting tools. The glass plate was then put into a distilled water and left to stand until a membrane layer formed. After that, the membrane was rinsed and placed in a vessel with distilled water.

### Table 1. Membrane compositions

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PES</td>
</tr>
<tr>
<td>MA-0</td>
<td>17.5</td>
</tr>
<tr>
<td>MA-0.1</td>
<td>17.5</td>
</tr>
<tr>
<td>MA-1</td>
<td>17.5</td>
</tr>
<tr>
<td>MS-1</td>
<td>17.5</td>
</tr>
</tbody>
</table>

### 2.3. FTIR Analysis

Functional group of the membranes has been analyzed by using the Fourier Transform Infrared (FTIR) (Shimadzu Prestige 6400) instrument. The membrane was cut (to a size of 4 × 4 cm) and dried before being placed on the object cell. The emitted light was then recorded in the FTIR instrument at a specific wavenumber and intensity. The spectra was used by measured in the 500–4000 cm⁻¹ wavenumber.

### 2.4. Membrane Morphology

The membrane morphology test aimed to determine the membranes surface morphology and cross-sectional structure. This analysis provided qualitative information about the range of membrane pores, distribution, and overall pore geometry. This analysis was carried out using SEM. The membrane was cut and dried in a freeze-dryer for 24 h to remove the water content in the membrane. Furthermore, the membrane was coated with platinum to produce electrical conductivity before being observed under a vacuum. Electron energy with a specific voltage (kV) was used to observe the morphology membrane.

### 2.5. Tensile Strength Analysis

This test aimed to determine the mechanical properties of the membrane, particularly the tensile strength. Tensile strength was determined by pulling the membrane with uniform dimensions and, using the stereograph as a tensile strength testing tool. Each analysis was carried out three times. The tensile strength of the membrane was calculated using Equation 1 (Febriasari et al., 2020).

\[
\sigma = \frac{F}{A_0}
\]  

Where \( \sigma \) was membranes tensile strength (MPa), \( F \) was the load, and \( A_0 \) was membranes surface area.
Elongation percentage of membrane was measured by following the Equation 2 (Febriasari et al., 2020).

\[ E = \left( \frac{\Delta L}{L_0} \right) \cdot 100\% \]  

(2)

\( E \) was the elongation percentage, \( \Delta L \) was the corrected extension of the, and \( L_0 \) was the membrane’s length.

2.6. Porosity Analysis

The total membrane porosity was calculated using Equation 3, which was based on the gravimetric method (\( \varepsilon \)).

\[ \varepsilon = \frac{W_1 - W_2}{\rho A l} \cdot 100\% \]  

(3)

Where \( W_1 \) was the weight of the wet membrane (g), and \( W_2 \) represented the weight of the membrane which was dried in an oven at 60°C (g). Furthermore, \( l, A, \) and \( \rho \) represented the thickness of the membrane (mm), the area of the membrane (cm²), and the density of water (0.998 g/cm³), respectively.

2.7. Membrane Filtration Performance

This test aimed to identify the permease performance membrane. Each membrane that has been fabricated was tested for permeability by flowing distilled water inside the dead-end module. This filtration was carried out at three different pressures, namely 1, 2, and 3 bar. The test was begun by compacting the membrane for 1 h. Then, data was taken in the form of permeate weight recorded for 90 minutes. Based on this data, the pure water flux value was obtained using Equation (4).

\[ J = \frac{Q}{A \cdot t} \]  

(4)

Where \( J \) was the pure water flux (L/m²·h), \( Q \) was the permeate volume (L), \( t \) was the filtration time (h), and \( A \) was the membrane surface area (m²).

3. Results and Discussion

3.1. Fly Ash Chemical Groups

Figure 1 illustrates the FTIR spectra of fly ash in the range of peaks from 4000 to 500 cm⁻¹. Fly ash displays an absorption peak at a wavenumber of 3600-3200 cm⁻¹, with a particular peak at 3317.56 cm⁻¹, indicating the presence of stretching OH bond vibrations. The absorption peak of functional groups containing the element Silica (Si) is discovered at a wavenumber of 1070–1170 cm⁻¹, showing the presence of stretching Si–O–Si bond vibrations. Furthermore, there are C–H bond vibrations at wavenumbers 2800–3000 cm⁻¹, resulting from organic impurities present during the production of fly ash samples or some of the hydrocarbons included in fly ash. The presence of high-intensity CO₂ in fly ash indicates the presence of C-related impurities, such as CO₂. A peak at 680.87 cm⁻¹ in the wave range of 800–400 cm⁻¹ indicates the presence of Al–O–Si stretching vibrations in fly ash (Rahmawati et al., 2021). According to the findings of the study on the functional groups of fly ash, there are three main components: iron (Fe₂O₃), silica (SiO₂), and alumina (Al₂O₃) (Ahmad et al., 2021).

3.2. Membrane Chemical Groups

Figure 2 shows the FTIR spectra of all prepared membranes. It reveals similar peaks in pure PES membranes and modified membranes. A peak in a pure PES membrane is formed by functional groups, which detects at 1576.74 cm⁻¹, most noticeably the C=C bond stretching of cyclic alkane. Peaks of 1295.93 cm⁻¹, 1238.00 cm⁻¹, and 1147.51 cm⁻¹ correspond to the sulfone group (S=O stretching). Furthermore, the wavenumbers of 1103.86 cm⁻¹ and 1071.50 cm⁻¹ indicate the presence of C–O stretching bonds, whereas wavenumbers of 870.27 cm⁻¹ and 834.55 cm⁻¹ indicate the presence of C=C stretching alkane bond vibrations.
similar to pure silica membrane (MS–1), indicating that silica particles from fly ash or pure silica have been successfully incorporated into the membrane matrix (Muhamad et al., 2015).

### 3.3. Membrane Porosity

Figure 3 shows the porosity of all fabricated membranes. From MA–0 to MA–1 and MS–1, the porosity tends to increase. However, MA–0.1 shows a lower percentage of porosity than MA–0. The pores produced on the MA–0.1 membrane are not equally distributed, resulting in a drop in the porosity value.

In addition, MA–1 and MS–1 also have higher porosity values than MA–0. Surprisingly, MA–1 has the highest total percentage of porosity. Fly ash modified to PES membrane has a higher porosity value than pure silica modified to PES membrane, which correlates to the correct pore distribution (MS–1).

### 3.4. Tensile Strength

Table 2 shows the mechanical properties of tensile strength and elongation of the pure PES membrane (MA–0) and modification membrane with fly ash 0.1 and 1 wt% (MA–0.1 and MA–1) and modification with silica 1% (MS–1). The tensile strength of the MA–0 membrane is 59.80 kgf/mm², which is lower than MA–0.1 and MA–1 membrane with 62.45 and 72.92 kgf/mm². The increase in the tensile strength value cannot be separated from the adsorption of polymer chains into the fly ash pore structure, when polymer absorbs into the pores of the fly ash, which has a large surface area, the polymer filler interactions increase, increasing tensile strength (Peydayesh et al., 2018). Pure PES membranes generally have low tensile strength values, but the tensile strength increases when fly ash additives are added. The membrane with silica has the tensile strength more increased with the additive fly ash.

The elongation of the membranes with fly ash as additive decreased with increase of the fly ash contents. But the silica in membrane still give the high elongation with the

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Tensile Strength (kgf/mm²)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA–0</td>
<td>59.80</td>
<td>26.43</td>
</tr>
<tr>
<td>MA–0.1</td>
<td>62.45</td>
<td>21.62</td>
</tr>
<tr>
<td>MA–1</td>
<td>72.92</td>
<td>18.48</td>
</tr>
<tr>
<td>MS–1</td>
<td>117.00</td>
<td>54.81</td>
</tr>
</tbody>
</table>

### 3.5. Membrane Morphology Structure

Figure 4 shows the results of surface structure and cross-section image. The MA–0.1, MA–1, and MS–1 membranes have denser surface structures and smaller pore diameters than the MA–0 membrane, indicating the membrane's pore size can be reduced by adding chemicals. Furthermore, adding additives can result in a rough membrane surface because of the production of additive nanoaggregate on the membrane surface. The prepared membrane has an asymmetrical structure with two layers, consisting of a thinner top layer with dense pores and a larger pore size that functions as a cross-section and provides resistance to the membrane, as
established by SEM observations of the cross-sectional structure of the modified membrane. The modified membrane layer (MA–1) is thicker than the MA–0 membrane. After modification, there was no significant difference in the membrane matrix since the change was carried out by coating the surface (Mulyati and Mulyasari, 2018). As a result, the membrane surface is the only part of the membrane that is affected.

![SEM images](image1)

Figure 4. SEM image of the membranes surface and cross section area

### 3.6. Water Flux Performance

The volume of permeate that flow through each unit area of the membrane at a particular time is called flux. Figure 5 shows that the water flux on the MA–0 and MA–0.1 membranes have lower flux values in general than the fluxes on the MA–1 and MS–1 membranes. The enhanced water flux was attributable to the membrane’s increased hydrophilicity, which was generated by adding a fly ash additive. Water diffuses faster through hydrophilic membrane pores than hydrophobic ones, increasing the water flow as shown in the similar result in SEM characterization (Mulyati and Mulyasari, 2018). Overall, the best performance is obtained by modifying 1% wt. of additive fly ash with PES membrane, where the MA–1 membrane increased by 71% of water flux than the MA–0 membrane and increased by 19% compared to MS–1.

![Graph of water flux](image2)

Figure 5. Pure water flux of all prepared membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Coefficient</th>
<th>Membrane category</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA–0</td>
<td>4.29</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>MA–0.1</td>
<td>2.56</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>MA–1</td>
<td>7.31</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>MS–1</td>
<td>2.28</td>
<td>Nanofiltration</td>
</tr>
</tbody>
</table>

Table 3. Membrane permeability coefficient

![Graph of water flux with different pressure](image3)

Figure 6. Water flux of all prepared membranes with different pressure

Figure 6 shows the water flux on a pure and modified PES membranes at 1–3 bar pressure. The water flux increases significantly as the pressure increases (Moradi et al., 2020). Overall, using the MA–1 membrane at a pressure of 3 bar demonstrated the best trend of water flux values. As indicated in Table 3, the permeability coefficient reflects the level of membrane performance, which shows that
the MA-1 membrane provides the best permeability coefficient compared to other membranes. The addition of fly ash as an additive in the PES membrane gives a higher hydrophilic property that affects the permeability value in the membrane prepared. The addition of fly ash not only improves the membrane’s porosity, but also gives more uniform surface pores, as shown in other analysis.

4. Conclusion

In this study, fly ash has been effectively utilized to fabricate PES-based membranes by nonsolvent-induced phase separation methods. The addition of fly ash significantly influences the membrane properties and filtration performance. The results obtained from the functional group and SEM analysis confirmed that fly ash has been successfully incorporated into the membrane matrix. The addition of fly ash 1% wt. (MA–1) also increases the porosity and the hydrophilicity of the membranes. Through the membrane filtration performance, it is shown that the water permeability improved up to 71% (MA–1) more than the pure PES membrane (MA–0) and increased by 19% compared to pure silica-modified PES membrane (MS–1). In addition, the MA–1 membrane at a pressure of 3 bar reached the best performance of pure water flux because of the improvements in membrane characteristics. It can be concluded based on these results that fly ash from the power plant industries can be effectively used to fabricate the potential nanofiltration membrane for wastewater separation applications.

References


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