Effect of solvents on the morphology and performance of Polyethersulfone (PES) polymeric membranes material for CO₂/CH₄ separation

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Abstract. Membrane technology has several advantages such as the ability to separate chemical species within compact plant footprints, low thermal energy requirements and simple process flow schemes. By optimizing the available materials and analysis, this work comes with the objective to synthesize the polymeric membrane, which has the best separation performance. In this work, three (03) membranes have been synthesized and a comparative analysis were conducted based on different types of solvent namely N, N-dimethylacetamide (DMAc), N, N-dimethylformamide (DMF), N-methyl-2-pyrrolidinone (NMP). In characterizing the synthesized membrane, Thermo Gravimetric Analysis (TGA), Field Emission Scanning Electron Microscopy (FESEM) and Fourier Transform Infrared Spectroscopy (FTIR) analysis were used. A comparative study was carried out to compare the effects of each solvent towards CO₂ separation performance.

1. Introduction

Gas separation membranes have gained great attention in different industries as compared to conventional separation technologies [1]. Consequently, many researchers have worked on the improvement of membrane performance with the effects of key performance parameters [2], [3]. One of the most important and effective parameter is solvent. The selection of solvent can affect the gas-permeation properties and the morphology of the membranes [4]. Various solvents, depending on their specific chemical and physical properties, interact differently with polymers, and these results in different morphologies [5]-[7]. The physical properties of the different solvents have been given in table 1.
Table 1. Physical properties of solvents [8, 9].

| Solvent name                  | Molecular formula | Mole weight (g/mol) | Molar volume (cm³/mol) | Boiling Point (°C) |
|------------------------------|-------------------|--------------------|------------------------|-------------------|
| N-methyl-2-pyrrolidinone (NMP) | C₅H₉NO            | 99.13              | 96.430                 | 202-204           |
| N, N-dimethylacetamide (DMAc) | CH₃CON(CH₃)₂      | 87.12              | 92.978                 | 164.5-166         |
| N,N-dimethylformamide (DMF)  | HCON(CH₃)₂        | 73.09              | 77.426                 | 152-154           |

The main objective of this work is to perform a comparative study on the morphology and gas permeation of dense PES membranes prepared from various solvents e.g. N, N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidinone (NMP). The high performance glassy polymer PES was selected as the membrane polymer. The repeating unit in the structure of PES possesses a certain degree of rigidity such that it has a glass transition temperature of 225°C. Field emission scanning electron microscopy (FESEM) and Thermo gravimetric analysis (TGA) were performed to characterize the membrane morphologies and correlated them to their gas-permeation results.

2. Experimental Procedures

2.1. Materials
A commercial grade polyethersulfone (PES), ULTRASON E6020P®, with good thermal and mechanical properties, was purchased from BASF chemicals, Germany. Three (03) solvents e.g. N, N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidinone (NMP) were supplied by Merck (Germany) and used without further treatment. Test gases (CH₄ and CO₂ > 99.9 %) were purchased from Gas walkers Sdn. Bhd, Malaysia.

2.2. Synthesis of Membranes
Pre-dried and known percentage of PES was dissolve in different solvents e.g. DMAc, DMF and NMP to prepare casting solution in a closed container. The casting solution was stirred for 24 hour at room temperature to completely dissolve the polymers followed by degassing for 30 minutes to remove the air bubbles formed during the mixing process. The casting knife was adjusted at 180-μm opening and the casting solution was poured onto a clean glass plate to cast the membrane films. The casted membranes were isolated in the vacuum oven at 90° C for the 24 hours. After drying process, the membranes were secured. After number of experimental attempts, the optimized compositions of casting solution are given in table 2.
### Table 2. Membrane compositions.

| Solvent | Polyethersulfone (PES) |
|---------|------------------------|
|         | (wt %) | (wt%) |
| NMP     | 83     | 17    |
| DMF     | 82.5   | 17.5  |
| DMAc    | 85     | 15    |

2.3. Characterization of Membranes
The morphological analysis of synthesized membranes was characterized by Field Emission Scanning Electron Microscope (VPFESEM, Zeiss Supra55 VP) and Thermogravimetric Analyzer (TGA) (Perkin Elmer Simultaneous Analyzer STA 6000) in order to investigate the thermal stability of membranes.

2.4. Gas Permeability Studies
The permeability of pure CO₂ and CH₄ gas across the membrane was recorded in the pressure range of 6-10 bar and room temperature. The CO₂ permeability was calculated according to the following formula:

\[
p = \frac{22414}{A} \times \frac{l}{(p_2 - p_1)} \times \frac{p_1}{RT} \times \frac{dV}{dt}
\]

where \( A \) representing membrane area (cm²), \( P_1 \) and \( P_2 \) are the feed and permeate pressure, respectively, \( R \) is the universal gas constant (6236.56 cm³cmHg/mol.K), \( T \) represents absolute temperature (K), \( dV/dt \) is the volumetric displacement rate (cm³/s) and 22,414 is the number of (STP) of penetrant per mole [9-11]. The schematic diagram of membrane module is shown in figure 1.

![Figure 1. Schematic diagram of membrane module [12.]](image)
3. Results and Discussion

3.1. Morphological Analysis
The cross sectional views of the PES-NMP, PES–DMF and PES-DMAc polymeric membranes are shown in figure 2(a-c), respectively. As it can be seen in figure 2, the dense symmetric cross-section of all membrane was observed. figure 2a shows the dense, non-porous structure of PES membrane. No voids were present in this magnification. figure 2b and 2c also illustrated dense and nonporous structure. It shows the compatibility of polymer and solvent.

Based on the cross-sectional images of the membranes, it confirmed that all the membranes are dense in structure. This means that permeate can diffuse through whether by pressure, concentration potential gradient. In this context, the permeate which was CO₂ diffuse through pressure gradient. On the other hand, when the values for thickness of each membrane were compared to each other, the thickness for PES-DMAc membrane is quite higher than the other two (2) membranes. Table 3 shows the summary of membranes and the thickness.

| Membranes     | Thickness, μm |
|---------------|---------------|
| PES-NMP       | 44.67         |
| PES-DMF       | 48.03         |
| PES-DMAc      | 124.4         |

Figure 2. FESEM micrographs of (a) PES-NMP (b) PES-DMF and (c) PES-DMAc polymeric membranes.

The membranes synthesized are having different thickness because of their different rates of solvent evaporation during the heating process. For instance, PES-DMAc membrane has very large thickness due to the low rate of solvent evaporation during heating process. To conclude, all concentration of solvents managed to form homogeneous compatible solution with PES polymer matrix.
3.2. Thermal Analysis
Figure 3 shows the weight loss of PES-NMP, PES–DMF and PES-DMAc polymeric membranes as a change of temperature. It was observed that TGA curve has two weight loss curves. The first weight loss may be due to a small quantity of the trapped solvent. It was observed that the amount of residual solvent is in the order of NMP > DMF > DMAc. The amount of solvent residue depends on drying temperature of the membrane and increases with the increase in boiling point of solvent [12]. The second weight loss was found that the membranes are stable up to 450 °C. This is due to the decomposition temperature of PES which around this temperature. From the curves, the thermal stability behavior for each membrane can be determined. For instance, the major weight loss for each membrane samples can be obtained and analyzed. The major weight loss might be due to the decomposition of main chains of the polymer. Thus, TGA can be used to get the decomposition temperature for each membrane. The decomposition temperature will determine until what temperature the membrane can withstand before start to degrade and can no longer be used. It will be an indicator whether the synthesized membrane can be used in industry condition or not.

![Figure 3. TGA spectra of PES-NMP, PES-DMF and PES-DMAc polymeric membranes.](image_url)

3.3. Gas Permeation Study
Based on the result obtained from gas permeability test, the gas permeance for each type of membrane samples decreasing as the pressure increase. This reflects the normal behavior for PES membrane. However, at certain pressure, the value of permeance for PES-NMP and PES- DMF membranes start to increase back. This is might be resulted from plasticization of the membrane. Plasticization causing the changes in structure of the membranes which allowing more permeate to pass through the membrane. It was observed that all polymeric membranes have higher values of selectivity at 2 bar pressure. It was also observed that PES-DMF shown higher selectivity at 2 bar pressure as compared to PES-NMP and PES-DMAc. In summary, plasticization increases the amount of free volume for the membrane which causing increase in diffusivity. However, for PES-DMAc membrane, there was no effect of plasticization as the
barrer continue to decrease when pressure increase. Summary for gas permeability results is shown in table 4.

| Pressure (bar) | $P_{CO_2}$ (barrer) | $P_{CH_4}$ (barrer) | Ideal Selectivity, $P_{CO_2}/P_{CH_4}$ | Membranes |
|---------------|----------------------|---------------------|--------------------------------------|-----------|
| 2             | 1.91                 | 0.80                | 2.40                                 | PES-NMP   |
| 4             | 1.35                 | 0.60                | 2.25                                 |           |
| 6             | 0.99                 | 0.48                | 2.06                                 |           |
| 8             | 1.17                 | 0.57                | 2.07                                 |           |
| 2             | 45.72                | 17.89               | 2.56                                 | PES-DMF   |
| 4             | 38.58                | 15.43               | 2.50                                 |           |
| 6             | 29.40                | 13.72               | 2.14                                 |           |
| 8             | 30.87                | 16.24               | 1.81                                 |           |
| 2             | 52.42                | 24.60               | 2.13                                 | PES-DMAc  |
| 4             | 38.10                | 19.99               | 1.95                                 |           |
| 6             | 31.34                | 17.76               | 1.76                                 |           |
| 8             | 25.79                | 13.78               | 1.87                                 |           |

4. Conclusion
In summary, PES was added in three different solvents to develop the polymeric membrane with CO$_2$ and CH$_4$ permeation properties. FESEM analyses confirmed the dense and no porous structure. TGA analysis revealed that the developed polymeric membranes are thermally stable up to 450$^\circ$C. The highest value of selectivity (2.56) was achieved by the PES-DMF membranes at operating condition of 02 bar and 25$^\circ$C. The result from permeability test indicating that PES-DMF and PES-DMAc displayed higher gas permeance unit (GPU) when compared to PES-NMP membrane. However, in term of membrane selectivity, all membrane samples displayed the same trend, which was decrease in selectivity as the pressure increase.

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