Minimizing Solvent Toxicity in Preparation of Polymeric Membranes for Gas Separation

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ABSTRACT: Toxic solvents such as dimethylformamide (DMF) are widely used for the preparation of polymeric membranes due to the strong dissolving power. Environmentally friendly solvents are available, but the developed membranes suffered from low performance due to the poor solubility of the polymer in the solvent. In this work, polyetherimide membranes were prepared using DMF with the addition of the biodegradable solvent γ-butyrolactone (GBL). Results show that mixing 75 wt % of DMF with 25 wt % GBL enhanced the membrane gas permeability toward hydrogen, methane, helium, carbon dioxide, and nitrogen. The overall permeability was increased by 9.6% compared to the permeability of the membrane made by 100 wt % DMF. Hydrogen-to-methane selectivity was also raised from 26.3 to 29.3.

1. INTRODUCTION

Interest in implementing green chemistry in industrial processes has increased remarkably in recent years. The concept aims to reduce energy consumption and minimize generated waste. This can be achieved by redesigning the process, for example, alternating feedstock or changing the solvents. Preparation of gas-separation membranes involves the use of toxic solvents like N-methylpyrrolidone (NMP) and dimethylformamide (DMF) because they can dissolve the polymer at room temperature. However, these solvents are reported to be harmful if they made contact with the eye or skin. The solvent may also damage the reproduction system or the unborn child as shown in Table 1. Furthermore, the solvents may harm the aquatic life; therefore, they need special treatment before disposal to the sewage system. Many researchers tried to substitute the toxic solvents with the green ones, but the selection critically affects the membrane performance as the solvent defined the physical structure. Therefore, the green solvents should have properties similar to the toxic ones in term of boiling point, viscosity, and solubility. For liquid separation, researchers managed to replace the traditional solvents with biodegradable ones. For example, methyl lactate (ML) was successfully changed from NMP for the preparation of cellulose acetate for water separation without a drop in performance. However, the case is different for gas-separation membranes because the formation of a dense layer is required instead of a porous one. The transport mechanism in dense membranes is based on the solution-diffusion model where the gas is adsorbed and dissolved at the membrane surface. After that, the gas diffuses through the membrane by means of free volumes. These volumes work similar to tiny pores, but they differ from physical pores as their shape and location can change based on the operating conditions.

Table 1. Hazard Statements of Traditional Solvents for Membrane Preparation

| solvent               | hazard statements                                      |
|-----------------------|--------------------------------------------------------|
| dimethylacetamide (DMA)| harmful in contact with skin                           |
|                       | harmful if inhaled                                      |
|                       | causes serious eye irritation                           |
|                       | may damage fertility or the unborn child                |
| dimethylformamide (DMF)| flammable liquid and vapor                             |
|                       | harmful in contact with skin                           |
|                       | harmful if inhaled                                      |
|                       | causes serious eye irritation                           |
|                       | may damage fertility or the unborn child                |
| N-methylpyrrolidone (NMP)| highly flammable liquid                      |
|                       | harmful if swallowed                                    |
|                       | causes severe skin burns and eye damage                 |
|                       | may damage fertility or the unborn child                |

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A previous study showed that nontoxic solvents such as ML, ethyl lactate, propylene carbonate, tributyl o-acetyl citrate, tributyl citrate, and triethyl phosphate failed to prepare a polyetherimide (PEI) membrane for gas separation due to the poor solubility even at an elevated temperature of 100 °C. Nevertheless, the green solvent γ-butyrolactone (GBL) dissolved PEI, but the solution was very viscous making it more difficult to cast. The researchers managed to prepare the PEI membrane from GBL, but unfortunately, the performance of GBL membranes, in term of hydrogen permeance, was extremely low compared to membranes prepared by NMP. This sharp drop in the performance was interpreted by the formation of a densified layer by GBL, which limited the gas diffusion.

Another approach to using the green solvents is by blending them with the toxic ones to reduce the human and environmental impact. The objective of this study was to investigate the possibility of mixing toxic and nontoxic solvents for the preparation of polymeric membranes to minimize the toxicity of the generated waste. In this paper, PEI membranes were prepared using a mixed solvent of DMF and GBL with different concentrations of 25, 50, and 75 wt % GBL, balanced with DMF. PEI was selected as a polymer because of the excellent thermal and mechanical stability. The polymer is also gas-permeable and has excellent permeability toward hydrogen, helium, and carbon dioxide. It has a chemical formula of (C₃₉H₃₀N₂O₆)ₙ with a molecular weight of 30,000 Da. Gas permeance and selectivity of the fabricated membranes were measured and compared to the membranes made by 100 wt % DMF. Characterization techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) had been utilized to observe any changes in the structure due to the addition of GBL to DMF. Hansen’s model was also used to study the equilibrium interaction between the solvents and the polymer.

2. MATERIALS AND METHODS

PEI membranes were prepared using the phase-inversion method and DMF as a solvent. DMF is an organic solvent with a chemical formula of C₅H₅NO. It is colorless with a fishy smell and has a high boiling point of 153 °C. DMF has been selected over NMP because in the previous study, PEI membranes prepared by NMP showed a lower permeability and selectivity. This suggests that DMF has a better interaction with the polymer, and the chain was more stretched with DMF. First, PEI pellets (Sigma-Aldrich) were added to DMF (99.8%, Sigma-Aldrich) to form a solution of 27 wt % PEI. The membrane was prepared initially with different concentrations of 23, 27, and 30 wt % PEI, but 27 wt % gave the best membrane performance. The solution was heated and mixed overnight to form a homogeneous solution. After that, the solution was poured on a glass sheet, and it was tape-casted to form a film with a thickness of 300 μm. Next, the glass was immersed in water to exchange the solvent and precipitate the polymer. The membrane was kept to dry overnight and then cut into a disc with 47 mm diameter. Before operation, the membrane was heated to 110 °C to remove the residual solvent. This procedure was repeated, but for mixed solvents, the following three concentrations were used: 75 wt % DMF–25 wt % GBL, 50 wt % DMF–50 wt % GBL, and 25 wt % DMF–75 wt % GBL. The membranes were also prepared using GBL alone (99%, Sigma Aldrich) for comparison.

GBL has been selected as an environmentally friendly solvent because it is biodegradable as it decomposes in water to γ-hydroxybutyric acid and then to carbon dioxide. It is a colorless liquid with a creamy odor and has a chemical formula of C₄H₆O₂ with a boiling point of 204 °C. GBL was used before as a nutritional supplement for weight loss and sleep; however, the chemical was banned by Food and Drug Administration (FDA) in 1990 because it can cause death if taken with alcohol. It should be noted that pure GBL is still harmful if it made contact with skin or eyes despite being biodegradable in water.

The morphology of the membranes was examined using an SEM (JEOL, JSM-IT300) with INKA Oxford instrumentation with a voltage of 20 kV. Prior to scanning, the membranes were immersed in liquid nitrogen for 5 min and then cut to obtain the cross-sectional area. After that, the samples were gold-coated using a sputter coater (Polaron, SC7620) with a current of 18–20 mA for 45 s.

The membranes were characterized using an SEM (JEOL, JSM-IT300) to examine the cross-sectional surface. XRD (PANalytical, Empyrean XE) was also utilized to determine the structure of the polymer and calculate the distance between the chains, which is known as d-space. After characterization, the membranes were evaluated for gas separation using a membrane permeation unit (Convergence Inspector Neptunus). The unit consists of a membrane cell and mass flowmeters as shown in Figure 1. Pure gases (Kuwait Oxygen & Acetylene Company, KOAC, 99.99%) such as hydrogen, methane, helium, carbon dioxide, and nitrogen were fed independently to the cell at a rate of 100 L h⁻¹ using a flowmeter. The feed pressure was set to 5 bar, and the temperature was constant at 25 °C. The unit measures the permeate flow rate (using a flowmeter), and the permeance was calculated by the following equation, in gas permeation unit (GPU):

\[ P (\text{GPU}) = \frac{V_p}{A \Delta P} \]

where \( V_p \) is the permeate volume flow rate (cm³ s⁻¹), \( A \) is the active membrane area of 12.6 cm², and \( \Delta P \) is the pressure difference across the membrane (cm Hg). Gas ideal selectivity was calculated based on the permeability of two gases. For example, for hydrogen-to-methane selectivity, the following equation was applied:

\[ \alpha_{H_2/CH_4} = \frac{P_{H_2}}{P_{CH_4}} \]
where $P_{H_2}$ and $P_{CH_4}$ are the permeabilities of hydrogen and methane, respectively. Separation of hydrogen from methane can represent hydrogen recovery from a refinery off-gas. The membrane performance for helium purification was measured by determining its selectivity to methane and nitrogen. Natural gas purification and flue gas treatment were demonstrated by measuring the selectivity of carbon dioxide toward methane and nitrogen, respectively.\(^{14}\)

$$d = \sqrt{[\delta_d(\text{solvent}) - \delta_d(\text{polymer})]^2 + [\delta_p(\text{solvent}) - \delta_p(\text{polymer})]^2 + [\delta_h(\text{solvent}) - \delta_h(\text{polymer})]^2}$$ (3)

For solvent mixtures, Bagley’s equation can be applied to calculate the components of the mixture\(^{16}\)

$$\delta_{d(\text{mixture})} = a\delta_{d(\text{solvent} \ a)} + b\delta_{d(\text{solvent} \ b)}$$ (4)

$$\delta_{p(\text{mixture})} = a\delta_{p(\text{solvent} \ a)} + b\delta_{p(\text{solvent} \ b)}$$ (5)

$$\delta_{h(\text{mixture})} = a\delta_{h(\text{solvent} \ a)} + b\delta_{h(\text{solvent} \ b)}$$ (6)

where $a$ and $b$ are the weight fractions of solvent $a$ and $b$, respectively. Relative energy difference (RED) is a parameter for predicting the solubility of the solvent and the polymer, and it can be calculated by\(^{17}\)

$$\text{RED} = \frac{d}{R_0}$$ (7)

where $R_0$ is the interaction radius of the sphere in the Hansen space. This radius is determined experimentally, and it is unique for the polymer. The solvent dissolving power increases as the RED value approaches close to zero.\(^{18}\)

3. RESULTS AND DISCUSSION

The produced membranes were tested for hydrogen, methane, helium, carbon dioxide, and nitrogen, and the permeability data is given in Table 2. It is clear that the membrane made by 50 wt % DMF, 50 wt % GBL gave the highest permeance of 23.4 GPU, which exceeded the membrane made by 75 wt % DMF and 25 wt % GBL however gave a lower permeance of 15.9 and 9.0 GPU, respectively. Similar to hydrogen, the membrane made by 75 wt % DMF and 25 wt % GBL gave the highest permeance toward methane, helium, carbon dioxide, and nitrogen.

Hansen’s solubility parameters were also used to study the molecular interaction between the solvents and the polymer. The model consists of three components: dispersion ($\delta_d$), dipolar intermolecular force ($\delta_p$), and hydrogen bond ($\delta_h$). These parameters present a three-dimensional sphere known as the Hansen space. The distance ($d$) between the solvent and the polymer can be then calculated based on the solubility parameters of the solvent and the polymer as follows:\(^{15}\)

Overall, the gas permeance increased by 9.6% compared to the permeance of the 100 wt % DMF membrane. In terms of ideal selectivity, the membranes made by GBL solely gave a low hydrogen-to-methane selectivity of 5.9; whereas, the 100 wt % DMF membrane showed a selectivity of 26.3. Again, the membrane made by 75 wt % DMF and 25 wt % GBL resulted in a selectivity of 29.3. The membrane also showed the maximum selectivity for hydrogen-to-nitrogen, helium-to-methane, helium-to-nitrogen, carbon dioxide-to-methane, and carbon dioxide-to-nitrogen as shown in Table 3. The results in Tables 2 and 3 were obtained twice to confirm the reliability of the data. Two samples were tested for each solvent composition. The error was within the acceptable range of $\pm 10\%$.

Compared to other researchers’ work with a similar experimental setup, the permeability and selectivity of the developed membrane of this study showed better results. For example, Shamsabadi et al. prepared PEI membranes with a concentration of 28 wt % using NMP.\(^{19}\) The membrane thickness was also 300 $\mu$m, but the membrane showed a low hydrogen permeance of 1 GPU at 5 bar with a hydrogen-to-methane selectivity of only 17.

The developed membranes were characterized by SEM to investigate any changes in the structure. The top surface of the membranes was examined, and it was free from defects such as holes and cracks. The images of the cross-sectional area are given in Figure 2, and the membrane made by 100 wt % GBL showed almost a totally dense layer; whereas, other samples showed a combined structure of a porous and a dense structure. It is known that the dense layer controls the membrane permeability and selectivity.\(^{20}\) Measurements of the dense layer of all membrane samples are given in Table 4. The 100 wt % GBL membrane has the highest thickness of 10.8 $\mu$m, and
this interprets the lowest gas permeability due to diffusion limitation. Furthermore, the change in porosity may also affect the gas permeance.

The poor interaction between the polymer and GBL solvent may prevent chain stretching and cause coiling leading to the formation of the densified layer.\textsuperscript{21} Other researchers also observed a drop in the permeability and selectivity when the membrane thickness was increased, and they related it to the change in the gas molecule enthalpy and entropy due to the change in void volume.\textsuperscript{22} On the other hand, the 100 wt % DMF membrane had a thinner layer of 7.7 μm; whereas, the membrane made by 75 wt % DMF and 25 wt % GBL had the lowest thickness of 6.9 μm. The reduction in thickness could be related to the increase in solvent viscosity as DMF has a viscosity of 0.9 cP, while GBL has a viscosity of 1.7 cP. Furthermore, it is reported that GBL has a higher interaction with water,\textsuperscript{23} and this may increase the exchange rate between the solvent and water to form a sponge-like structure with uniform medium-sized holes (Figure 2b). In membrane processes, reducing the thickness of the dense layer is generally favorable as it gives the maximum permeability and selectivity due to the absence of diffusion and solubility limitations.\textsuperscript{24}

Other researchers also noticed an improvement in the permeability of the PEI membrane when the thickness of the densified layer was reduced.\textsuperscript{25} It was related to the high solubility of carbon dioxide due to the interaction with the polymeric chain. Furthermore, the lower kinetic diameter of carbon dioxide compared to nitrogen also enhanced the permeance. The change in thickness may also alter the crystallinity level, crystallinity orientation, and the number of free volumes.\textsuperscript{26}

Samples were additionally analyzed by XRD, and data is given in Figure 3. Samples made from 100 wt % GBL, 25 wt % DMF–75 wt % GBL, and 50 wt % DMF–50 wt % GBL show a very high intensity indicating that the structure is more crystallized. Some researchers noticed that the higher the

Table 4. Thickness of the Dense Layer of the Developed PEI Membranes

| sample | thickness (±0.1 μm) |
|--------|---------------------|
| 100 wt % DMF | 7.7 |
| 75 wt % DMF, 25 wt % GBL | 6.9 |
| 50 wt % DMF, 50 wt % GBL | 8.3 |
| 25 wt % DMF, 75 wt % GBL | 9.9 |
| 100 wt % GBL | 10.8 |
intensity, the lower the permeance due to the limitation in molecular diffusion. This finding also matches the results in this study where enriched GBL membranes suffered from the low permeance. For the sample prepared by 75% DMF and 25% GBL, the intensity is slightly higher than the intensity of the 100% DMF membrane. Therefore, it was expected to see a drop in the membrane permeance in the 75% DMF–25% GBL membrane; however, the slight increase in intensity is actually reported to enhance the permeance due to the increase in the interfacial space between the amorphous and crystalline structure.

XRD was used as well to calculate the distance between polymer chains (d-space). The data is given in Table 5, and changing or mixing the solvents did not alter the d-space value. Some researchers also noticed that the d-space value did not change when the solvent was altered.

Table 5. Calculated Distance between Polymer Chains (d-Space) in the PEI Membrane

| Sample            | d-space (Å) |
|-------------------|-------------|
| 100% DMF          | 4.15        |
| 75% DMF, 25% GBL  | 4.15        |
| 50% DMF, 50% GBL  | 4.16        |
| 25% DMF, 75% GBL  | 4.16        |
| 100% GBL          | 4.15        |

Hansen’s solubility parameters were used to calculate solubility of solvent mixtures with the polymer using eq 3–7. The data is given in Table 6. Using a pure DMF solvent gives a RED of 1.1, while using pure GBL, RED increased to 1.5. This confirms that the solubility of GBL is less than that of DMF, and this may interpret the low performance of GBL membranes. For the 75% DMF–25% GBL membrane, which shows the highest performance in terms of permeability and selectivity, RED slightly increased to 1.2. It should be noted that, in RED calculations, the solvent is considered as a “good solvent” when the value is higher than the unity. However, in this study, all the values are over the unity. This does not automatically mean that DMF is a poor solvent as the Hansen’s model does not take some properties in consideration such as temperature, polymer morphology, and solvent molecular size. Experimental work is necessary to confirm the reliability of Hansen’s results.

In the environmental point of view, the solution of 75 wt % DMF and 25 wt % GBL is considered toxic and harmful to aquatic life because it is still concentrated with DMF. It was difficult to use GBL alone to form PEI membranes because of the low permeance and selectivity. Other eco-friendly solvents should be tested to seek the possibility of substituting DMF.

4. CONCLUSIONS

Preparation of polymeric membranes generally involves the use of toxic solvents such as DMF due to the strong dissolving power. However, special care is needed when handling these solvents due to possible skin and eye irritation. Furthermore, the solvents will require a chemical treatment before disposal to prevent harm to aquatic life. Many researchers tried to substitute the toxic solvents with environmentally friendly ones, but the fabricated membranes had a lower gas permeance and selectivity. In this work, the nontoxic solvent GBL was mixed with DMF with three different concentrations of 25, 50, and 75 wt % GBL, balanced with DMF. The developed membranes were tested for separation of various gases such as hydrogen, methane, helium, carbon dioxide, and nitrogen. It was found that the membrane made by 75 wt % DMF and 25 wt % GBL had the best permeance and selectivity. The addition of GBL to DMF improved hydrogen permeance from 20.8 to 23.4 GPU with an increase in hydrogen-to-methane selectivity from 26.3 to 29.3. Characterization techniques such as SEM revealed that adding 25 wt % GBL to DMF reduced the thickness of the selective layer from 7.7 to 6.9 μm. The membrane improvement was also linked to the increase in XRD intensity as the structure becomes more crystallized. Furthermore, the addition of GBL changed the viscosity and raised the interaction with water, and this resulted in formation of a sponge-like structure, which facilitated the gas diffusion.

Hansen’s model was also used to predict the solubility parameters of the mixture solvents, and the model reported that GBL has a lower solubility with PEI. This matched the experimental data as GBL membranes suffered from the lower performance. However, Hansen’s model did not give key information on the 75 wt % DMF–25 wt % GBL membranes as the RED value slightly increased from 1.1 to 1.2. This was connected to the limitation of the model as it did not take in consideration the temperature, molecular size, and polymer morphology.

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