

Enhanced Gases Separation of Cellulose Acetate Membrane Using N-Methyl-1-2 Pyrrolidone as Fabrication Solvent

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ABSTRACT

Among the various polyimides, cellulose acetate (CA) as the membrane material in the market of gases separation processes is extensively used. However, CA membrane demonstrates relatively low CO₂ permeability and low CO₂/N₂ and CO₂/CH₄ gas pair selectivity. Besides, fabrication of defect-free CA membrane challenging, and fabrication solvent control the non-selective voids of the membrane. Although, there were few studies reported on the development of CA membrane using various solvents; the fabrication of CA membrane using methyl-2-pyrrolidone (NMP) is scarcely reported in the literature and detailed investigation is needed. Thus, the objective of the present work is to fabricate CA membrane using NMP solvent. Analytical tools have verified the structure, morphology and bond vibration of the resultant membrane, respectively. The resultant CA membrane showed the CO₂ permeability, CO₂/CH₄ and CO₂/N₂ ideal selectivity of 15.56 Barrer, 10.71 and 8.80, respectively. The performance of the resultant membrane was found higher the previously reported studies for CA membrane fabricated using different solvents. Thus, it can be concluded that the NMP is effective solvent and it can be recommended to use a solvent for fabrication of other types of membranes.

Keywords: Cellulose acetate (CA), membrane, fabrication, gases separation, N-Methyl-2-pyrrolidone (NMP).

INTRODUCTION

The rise of CO₂ concentration in the atmosphere is the main culprit for the climate change and global warming [1]. CO₂ separation using membrane process is highly attractive compared to other conventional separation technologies because of their features including low cost, ease of maintenance, smaller footprint, and low labor intensity [1-7]. These benefits endow the membrane as a significant and competitive technology for CO₂ separation [8, 9]. Therefore, fabrication of membranes in gases separation is increasing tremendously. Typically, inorganic membranes possess a number of limitations including, high fabrication cost and complex fabrication procedure [8, 9]. On the other hand, mixed matrix membranes (MMMs) still facing severe challenging tasks including, poor compatibility between inorganic filler with the polymer matrix and particles agglomeration [10, 11]. The successful application of polymeric membranes in the CO₂/N₂ and CO₂/CH₄ separation is mainly due to economical processing capabilities and high mechanical stability [3, 12]. Polymers include cellulose acetate (CA), polysulfones (PSF), polyimides (PI), silicone rubber,

polyphenylene oxide are commonly used for CO₂/N₂ and CO₂/CH₄ separation [13]. On the basis of materials, there are two types of polymeric membranes which include; glassy and rubbery polymers. From the literature, it has been found that the glassy polymers demonstrated higher perm-selectivity and higher chemical resistance compared to rubbery polymers [14]. Furthermore, among the glassy polymers, polyimides demonstrated better performance in CO₂/CH₄ separation.

Among the various polyimides, inclusive use of CA material in the market of gases separation processes is mostly because of its low manufacturing cost, good toughness, and virtuous compatibility. In addition, CA polymer demonstrated good fouling resistance, ease of processability and high CO₂ solubility [15, 16]. Thus, various researchers reported on the fabrication of CA membrane for gases separation [15-18]. Recently, acetone has been used by the Carine et al. [17] as a solvent for fabrication of CA membrane. They found that CO₂ permeability of 6.1 Barrer and CO₂/CH₄ selectivity of 5.08 were achieved. Consequently, Seng et al. [18] reported the performance of CA membrane fabricated using THF solvent. CO₂ and N₂ permeability of 4.55 and 1.0 Barrer were obtained, respectively. Meanwhile, the CO₂/N₂ selectivity of 4.55 was achieved.

On the other hand, as reported in the literature, the fabrication of polymeric membranes using NMP solvent usually resulted in the polymeric membrane with improved fractional free volume and thus, enhanced the gases permeation performance [19]. In 2011, Sikander and his coworkers [20] studied the NMP/DCM composition effect on the permeation performance of PSF membrane for CO₂ removal from CH₄. They observed that the CO₂ permeability was increased with the increase of NMP concentration in the NMP/DCM solution and thus, CO₂/CH₄ gas pair selectivity was increased from 19 to 26. Recently, Chung et al. [21] reported the fabrication of 6FDA-durene membrane using NMP solvent. They obtained a CO₂/CH₄ selectivity of 16.59 which was 137 % higher compared to the selectivity reported for 6FDA-durene membrane fabricated using DCM solvent [22]. These results are mainly because of NMP solvent which enhances the hydrogen bonding between OH- groups of polymers. Thus, non-selective voids reduced and the gases selectivities increases. In addition, longer evaporation time of NMP solvent during membrane fabrication also contributed to the enhancement of the CO₂ permeability. With longer evaporation duration, polymer chains tend to rigidified and thus, enhanced the penetration of gases through the resultant membrane [19].

Among the various reported CA membrane; the fabrication of CA membrane using NMP is yet to be investigated. Therefore, in the current study, we had reported the fabrication of CA membrane using NMP solvent. Subsequently, the structure, morphology and bond vibration of the resultant CA membrane is investigated by using XRD and FESEM, respectively. Lastly, the permeation performance of resultant CA membrane in CO₂/CH₄ and CO₂/N₂ separation is evaluated.

EXPERIMENTAL METHOD

Materials

Cellulose acetate (CA) was purchased from Sigma Aldrich (Malaysia). N-methylpyrrolidone was purchased from Merck (Malaysia). Polymer and solvent were used as

received. Table 1 shows the physicochemical properties of the CA polymer and NMP solvent used in the present study.

Table 1: Physicochemical properties of CA polymer and NMP solvent used in the present study [21, 22].

Physicochemical properties	CA	NMP
Density (g/cm ³)	1.30	1.03
Boiling point (°C)	NA	204
Appearance	White powder	Colorless liquid
Solubility	Organic compounds	Organic/inorganic compounds

Fabrication of CA Membrane

In the current work, solution casting method was adopted in order to fabricate pristine CA membrane as described in the literature [23]. CA was mixed into NMP solvent in order to CA/NMP solution. Then, CA/NMP solution was stirred for 18 h and the concentration of CA was maintained at 10 wt% in the solution. Then, CA solution was degassed for 12 h. After that, CA solution was cast on Petri dish and it was preceded for drying in an oven at 90 °C for 24 h. In the next step, the resultant membrane was subjected to the annealing. Annealing of the membrane was conducted under the vacuum condition at 90 °C for 24 h with a heating rate of 10 °C/12 h.

Characterization of CA Membrane

In the current work, XRD (PANalytical) was used to determine the structure of the resultant membrane. XRD was operated at 2 theta range from 5° ≥ 2θ ≥ 45°. Subsequently, surface morphology, cross-sectional view, and thickness of the membrane were measured using FESEM (Zeiss Supra 55 VP). Firstly, the membrane was placed into the FESEM chamber and it was operated at 5 kV under vacuum condition. Subsequently, the presence of functional groups and chemical bonds in CA membrane were determined by using ATR-FTIR (Perkin-Elmer Spectrum one). The resultant membrane was scanned for wavenumbers ranging from 400 cm⁻¹ to 4000 cm⁻¹ under the continuously purged N₂.

Gases Permeation Measurement

The permeation performance of the resultant CA membrane was evaluated by determining the CO₂, N₂, and CH₄ permeability as well as CO₂/N₂ and CO₂/CH₄ gas pair selectivities. The design of the permeation test rig has been reported in our previous proceeding [24]. CA membrane was installed in the permeation cell and it was preceded to vacuum for 12 h in order to remove the moisture. In the next step, feed gases were injected to the equipment and their pressure was maintained at 3 bar. Subsequently, feed flow rate of gases was 200 mL/min. The data was produced with an error of ± 3%. The gases permeability of the membrane was determined by using Eq. (1) [25]:

$$\frac{P_{CO_2}}{L} = \frac{Q}{A\Delta P} \quad (1)$$

Where the CO₂ permeability of the CA membrane has been presented as P_{CO_2} with units of Barrer. Meanwhile, gases flow rates and their pressure drop are shown using the symbol of Q and ΔP , respectively. Subsequently, CO₂ and CH₄ permeabilities of the membrane were divided in order to calculate the CO₂/CH₄ ideal selectivity of the CA membrane as in Eq. (2) [25]:

$$\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \quad (2)$$

RESULTS AND DISCUSSION

X-ray Diffraction (XRD)

XRD pattern of the resultant CA membrane is presented in Figure 1. Referring to Figure 1, it has been found that resultant membrane possesses the amorphous structure because no substantial peak is obtained in their XRD pattern. This result was mainly because of non-crystalline nature of the CA polymer. Subsequently, similar, XRD pattern has been reported by the Sanaeepur et al. [16] for CA membrane.

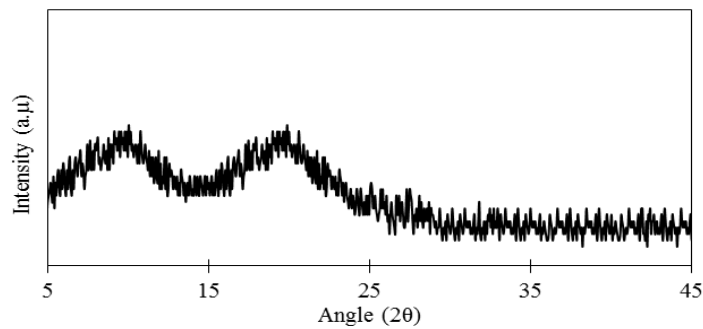


Figure 1. XRD pattern of resultant CA membrane.

Field Emission Scanning Electron Microscopy (FESEM)

Surface and cross-sectional view of the CA membrane are shown in Figure 2. Referring Figure 2 (a), resultant membrane shows uniform and smooth surface morphology. Referring to Figure 2 (a), the inner structure of the membrane is also homogeneous [26]. Subsequently, it has also been found that there were no obvious voids formed in the resultant membrane. This result could be due to the bonding between OH- vibrations of the hydroxyl group of CA polymer. Hydrogen bond has been produced by the effect of NMP. Besides, longer evaporation time of NMP also contributes to the slow settling of the polymer and thus it restricted the neighboring C-OH rings. Thus, no micro-voids are produced in the membrane [19].

Fourier transform infrared (ATR-FTIR)

ATR-FTIR analysis of the resultant CA membrane is shown in Figure 3. From Figure 3, it has been found that the resultant membrane showed the characteristics peaks at 660 cm⁻¹, 900 cm⁻¹, 1032 cm⁻¹, 1121 cm⁻¹, 1215 cm⁻¹, 1367 cm⁻¹, 1431 cm⁻¹, 1737 cm⁻¹ and 3475 cm⁻¹ [18]. The characteristic peak at 660 cm⁻¹ is due to the aromatic C-OH bond

polymer chain. However, the peak at 900 cm^{-1} endorses the β link [16]. Meanwhile, the broad peaks at 1032 cm^{-1} and 1121 cm^{-1} are corresponding to the skeletal movement of C-O bond. Subsequently, significant peaks at 1215 cm^{-1} , 1367 cm^{-1} , 1431 cm^{-1} and 1737 cm^{-1} are mainly due to the C-C-O bonds, CH_3 symmetric vibration and C=O stretching, respectively [27]. Moreover, peak at 3475 cm^{-1} endorses OH- bond of the of CA membrane [27, 28].

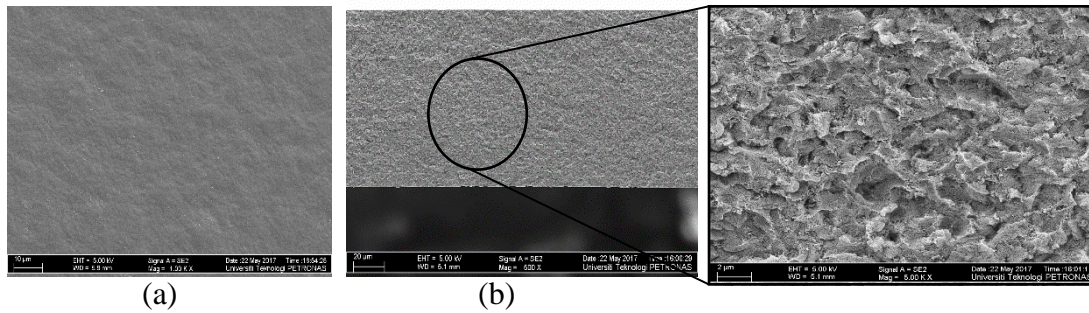


Figure 2. FESEM images of (a) surface and (b) cross-sectional view of CA membrane.

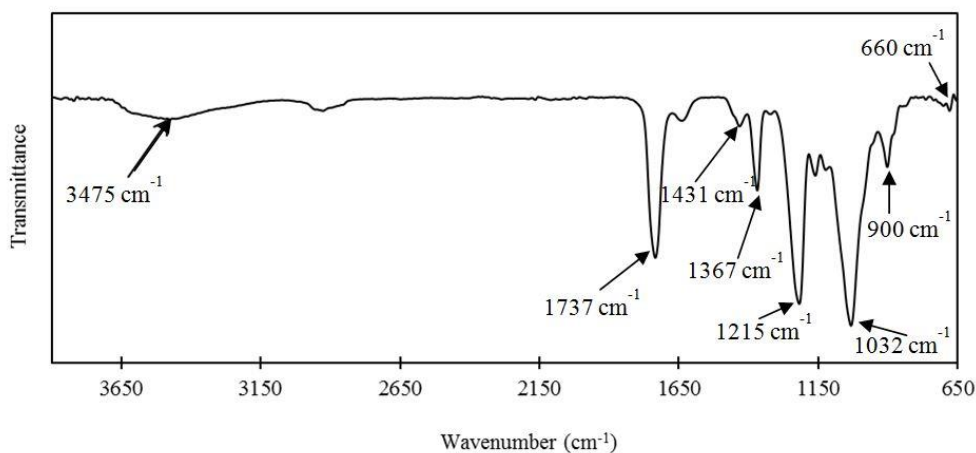


Figure 3. ATR-FTIR analysis of resultant CA membrane.

Gas Permeation Study and Comparison with The Literature Results

Figure 4 shows the permeation performance of resultant CA membrane. Referring to Figure 4, it has been found that CO_2 permeability is higher than that of those values obtained for N_2 and CH_4 gases. Furthermore, gases permeabilities are decreasing in the order of $\text{CO}_2 > \text{N}_2 > \text{CH}_4$. This decreasing trend is could be due to the solubility difference of gases in the CA matrix [15]. From Figure 4, it can also be seen that the gas pair selectivities of 10.71 and 8.80 are obtained for the resultant CA membrane, respectively. It is interesting to note that, the gas pair ideal selectivities are also decreasing in the order of $\text{CO}_2/\text{CH}_4 > \text{CO}_2/\text{N}_2$. This result is attributed to the lower CH_4 Langmuir sorption of CH_4 compared to the N_2 [17]. Therefore, CH_4 permeability is smaller than N_2 permeability over the resultant CA membrane. Hence, CO_2/CH_4 gas pair ideal selectivity is higher than that of CO_2/N_2 gas pair ideal selectivity over the CA membrane.

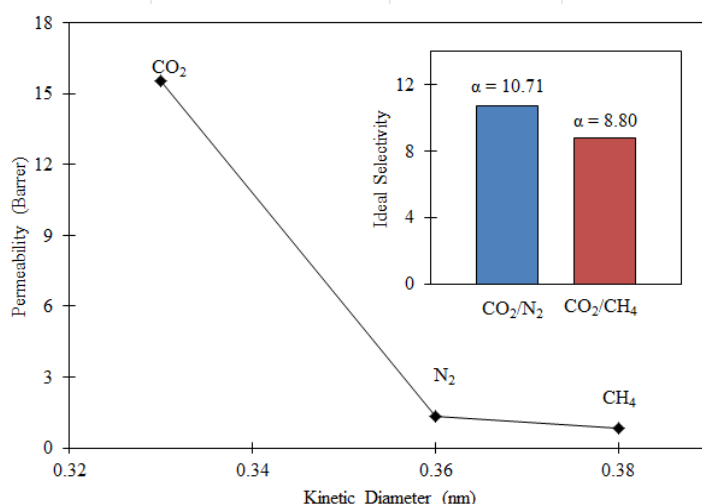


Figure 4: Permeation performance of resultant CA membrane.

Meanwhile, Table 2 shows the comparison of CO₂/N₂ and CO₂/CH₄ ideal selectivities of CA membrane fabricated in the current study with the reported literature. Referring to Table 2, it has been found that the permeation performance of the resultant CA membrane was higher than those values achieved for CA membrane fabricated using THF and acetone solvents [15, 18, 29]. This result could be because of NMP solvent which enhanced the hydrogen bonding between OH⁻ vibrations of the hydroxyl group and restriction of neighboring C-OH rings and thus, increased the rigidity of the polymer chain as well as the gas permeation performance. Besides, longer evaporation time of NMP solvent during membrane fabrication also contributed to the enhancement of CO₂ permeability. With longer evaporation duration, polymer chains tend to rigidified with higher free volume and it contributes to enhance the diffusion of gases through the resultant CA membrane [19]. In the present work, CO₂ permeability and gas pair ideal selectivities of the CA membrane were increased about 158 % and 42.3 %, respectively compared to the reported literature [15]. Overall, the gas permeation performance has been enhanced using CA membrane fabricated via NMP solvent.

Table 2: Comparison of CO₂/CH₄ and CO₂/N₂ ideal selectivities of CA membrane fabricated in the present work with reported literature.

CO ₂ permeability (Barrer)	N ₂ permeability (Barrer)	CH ₄ permeability (Barrer)	CO ₂ /CH ₄ selectivity	CO ₂ /N ₂ selectivity	Solvent	Ref.
15.56 ± 1	1.77 ± 0.5	1.45 ± 0.5	10.71 ± 0.5	8.80 ± 0.5	NMP	This work
1.08	0.44	0.26	4.15	2.45	THF	[15]
6.10	-	-	5.08	-	Acetone	[17]
4.55	1.00	-	-	4.55	THF	[18]
0.17	0.12	0.18	0.94	1.44	THF/EtOH	[29]

CONCLUSION

In this work, CA membrane has been fabricated using NMP solvent and its structural properties have been verified using analytical tools. Subsequently, CO₂ permeability, CO₂/CH₄ and CO₂/N₂ ideal selectivities of 15.56 Barrer, 10.71 and 8.80 were achieved, respectively. Consequently, permeation performance of the resultant CA membrane was higher than those values achieved for previously fabricated CA membrane. Higher permeation performance of resultant CA membrane could be because of NMP solvent which enhanced the hydrogen bonding between OH⁻ vibrations of the hydroxyl group and restriction of neighboring C-OH rings and thus, increased the rigidity of the polymer chain as well as the gas permeation performance. Therefore, CO₂ permeability and selectivities of resultant CA membrane were increased about 158 % and 42.3 %, respectively compared to the reported literature. Overall, the gas permeation performance has been enhanced using CA membrane fabricated via NMP solvent. Therefore, CA membrane fabricated in the current work has a potential for industrial gas separation.

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