

P84/Zeolite-Carbon Composite Mixed Matrix Membrane for CO₂/CH₄ Separation

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Abstract: Mixed Matrix Membranes (MMMs) which consist of 0.3 wt.% Zeolite-Carbon Composite (ZCC) dispersed in BTDA-TDI/MDI (P84 co-polyimide) have been prepared through phase inversion method by using N-methyl-2-pyrrolidone (NMP) as a solvent. Membranes were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Thermogravimetric Analysis (TGA), and Fourier Transform Infrared (FTIR). Membrane performance was measured by a single gas permeation of CO₂ and CH₄. The maximum permeability of CO₂ and CH₄, which up to 12.67 and 6.03 Barrer, respectively. P84/ZCC mixed matrix membrane also showed a great enhancement in ideal selectivity of CO₂/CH₄ 2.10 compared to the pure P84 co-polyimide membrane.

Keywords: mixed-matrix membrane; carbon-zeolite composite; gas separation

■ INTRODUCTION

Natural gas is an important natural source of fuel. Natural gas mostly contains hydrocarbon especially methane (CH₄) with small amount impurities of N₂ and CO₂ [1]. Higher purity of CH₄ is required for an energy source since both N₂ and CO₂ decrease the heating value. Furthermore, CO₂ is corrosive in the presence of moisture. Thus, removing impurities such as CO₂ in raw natural gas is necessary.

The development of gas separation by membranes technology increased rapidly in the last two decades. The technology offers ease operation, low energy requirement and the overall economies of low-scale operation [2]. Polymeric membranes are the most used material for gas separation membrane. However, it has limitation such as poor thermal and chemical resistance [3]. Choosing proper polymer precursor is necessary to avoid these drawbacks. Polyimides are one of the most preferred polymers used in the membrane community [4-11]. Polyimides are a polymer with high thermal properties

(T_g~300 °C). Furthermore, they are affordable, good mechanical properties and ability to be modified in a different configuration (*flat, hollow fiber, supported*). In addition, this polymer is one of the best precursors for preparing carbon molecular sieve membranes [3,7,12-13].

On the other hand, advance membrane preparation such as polymer blend and composition are new promising field due to enhancing the thermal, mechanical and separation properties of the membrane. The composition of polymer with inorganic filler is the most efficient way to improve the overall membrane performance [14]. This field continues to receive a lot of interest recently due to offers significant improvement performance of membrane such as good separation factor, mechanical strength, thermal and chemical stability [15]. Many types of fillers already reported previously such as zeolite [16], silica [17], Metal Organic Framework (MOF) [18] and Carbon Molecular Sieve (CMS) [19]. The problem that usually appears by

incorporating an inorganic filler into the polymer matrix is a void formation that leads to performance slump due to incompatibility. The incompatibility issue could be fixed by utilizing light weighed inorganic filler such as from carbon. Thus, developing a new filler is necessary.

In this study, the zeolite-carbon composite was used as filler material into BTDA-TDI/MDI (P84) co-polyimide. The filler can be acquired during the synthesis of zeolite template carbon. The use of zeolite as a filler in the membrane is quite widely studied, however in this research, we conduct a modification in zeolite pore by coating with carbon that coming from the impregnation of sucrose as a carbon precursor. The background that leads us to modify as such is due to the interaction of CO₂ and alkali zeolite occurs with CO₂ in linear orientation by ion-dipole interaction [20]. Furthermore, the affinity of CO₂ on alkali zeolite improves at a moderate temperature (~120 °C) due to less gas competitor, especially moisture [20]. However, if we apply such condition into polymeric membrane application, the membrane will suffer due to low thermal resistance. Moreover, at STP condition, the presence of moisture is abundant and could lead to the formation of hydrogen bonding with the oxygen species in the Si-O-Al structure of the zeolite. This will result in reduced permeation rate of CO₂. That is why, in this research, we coat the zeolite pore wall with material that has less hydrophobicity but still maintains the permeation rate of CO₂. One of the material is carbon that can be prepared through the impregnation of carbon precursor into zeolite pore.

The zeolite used in this research is zeolite-Y (NaY), which widely known as good for natural gas-related application and the carbon precursor is sucrose due to high carbon residue and widely available [21-23]. Our motivation utilizing this material as a new filler for polymer membrane is due to the high microporosity that could improve the gas selectivity, pore regularity to improve permeability and fixing compatibility issue. The membrane will be fabricated in the flat sheet using inversion phase method. The characterization of the membrane including morphology (SEM), topology (AFM), Fourier Transform Infrared (FTIR) and thermal stability (TGA) was conducted to study the properties of

the membrane as well as the membrane separation performance on CO₂/CH₄ separation.

■ EXPERIMENTAL SECTION

Materials

Zeolite-Y and zeolite-carbon composite

Sulfuric acid (H₂SO₄, 98%) were purchased from Merck. Sodium aluminate (NaAlO₂, Sigma Aldrich) were used as aluminate and sodium source for zeolite formation. Sodium silicate (Na₂SiO₃, Sigma Aldrich) were used as silicate and sodium source and Sodium Hydroxide (99% NaOH, pellet) were purchased from Sigma Aldrich for additional Sodium source and as the counter ion of zeolite. Sucrose (98%, Fluka) was used as a carbon source for zeolite-carbon composite.

Membrane

Polyimide BTDA-TDI/MDI (P84 co-polyimide) purchased from HP Polymer GmbH was selected as polymer precursor. P84 co-polyimide was dried at 100 °C overnight to remove any moisture prior to membrane preparation. N-methyl-2-pyrrolidone (NMP) purchased from Merck was selected as a solvent.

Synthesis Method

Zeolite-Y and zeolite-carbon composite

The overall synthesis method for preparing zeolite and zeolite-carbon composite can be seen in Fig. 1. Zeolite-Y was synthesized via hydrothermal of zeolite seed crystals. The molar composition of the gel was 1.0 NaAlO₂: 18 Na₂SiO₃: 1.75 NaOH: 23.33 H₂O. The gel was prepared by dissolving NaOH and NaAlO₂ into DI water. The solution was stirred at room temperature until homogenous aluminate solution obtained. Then Na₂SiO₃ was added drop wisely into the aluminate solution and stirred for 20 min. The solution was then moved into a stainless steel autoclave and aged for 1 day. The hydrothermal reaction was conducted in an oven at 100 °C for 7 h. The zeolite was then filtered and washed until the pH of filters reach < 9 and followed by drying at 110 °C for 24 h. White powder zeolite mass was then measured and stored in a desiccator for the next purpose.

Synthesized zeolite-Y was used as a template for

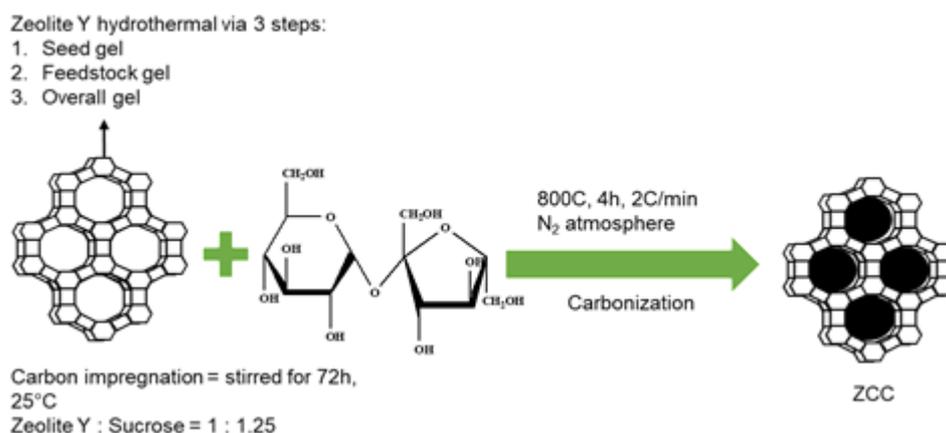


Fig 1. Schematic diagram of zeolite-carbon composite and ZCC preparation

zeolite-carbon composite. The zeolite-carbon composite was synthesized via the impregnation method. Zeolite-Y was degassed at 200 °C for 4 h inside a homemade tubular furnace with the heating rate of 1 °C/min to remove any adsorbed gasses prior to impregnation process. The mass ratio of zeolite-Y and sucrose was 1:1.25. The impregnation process was carried out by dissolving sucrose into 50 mL H₂SO₄ 0.35M, then followed by the addition of degassed zeolite Y and the solution was stirred at 250 rpm for 72 h in room temperature. The solution was then filtered and its residue (impregnated zeolite) moved into tubular holder prior to the carbonization process. The pyrolysis process was conducted inside a homemade tubular furnace at 800 °C for 4 h with a heating rate of 2 °C/min and under an N₂ flow of 30 cm³/min. The zeolite-carbon composite was then ground to obtain fine powder and store inside a desiccator for future treatment.

Membrane preparation

The dope solution (100 mL) consist of 12/88 wt% of P84 co-polyimide/NMP. ZCC was 0.3 wt% ratio to the dope solution. Zeolite-carbon composite were dried at 100 °C overnight prior to the membrane preparation to remove moisture. 0.3 wt% of ZCC was dispersed in NMP by sonication for 1 h. A total of 12 wt% of P84 were added to the mixture slowly and stirred with a mechanical stirrer for 24 h at 80 °C. The dope solution was then sonicated to remove the existing bubble. The dope solution was directly cast onto the clean glass plate to fabricate a mixed matrix membrane, followed by immersion in water to perform the phase inversion process. The membranes

were dried at room temperature for 24 h to remove the excess water.

Material characterization

X-Ray Diffractogram (XRD) was utilized to confirm the structure formation of zeolite-Y and zeolite-carbon composite. The pore properties of zeolite and zeolite-carbon composite were measured using Surface Area and Porosity Analyzer (Micromeritics, ASAP 2020). The gas used for adsorptive analysis was N₂ at a temperature of -195 °C. The morphology of each sample was observed using Scanning Electron Microscope (SEM) (Hitachi, TM 3000) with a potential of 15 kV and samples were coated with platinum. The sample thermal stability was characterized using thermal gravimetric analysis (TGA). The alterations in sample weight during the continuous heating process were recorded by TGA. The samples were heated from room temperature to 900 °C, at a heating rate of 10 °C/min with a nitrogen flow rate of 20 mL/min.

Pure gas permeation test

The CO₂ and CH₄ gases used in this permeation test were in UHP quality. The membranes were cut into circle shape membrane with a diameter of 5.7 cm. The single gas permeability was conducted at room temperature and pressure of 4 bar. The data measurement was taken by measuring the time for permeate gas required to reach 10 mL. The gas volume was measured using a bubble flow meter. The measurement was repeated 10 times. Permeability was calculated using Equation 1.

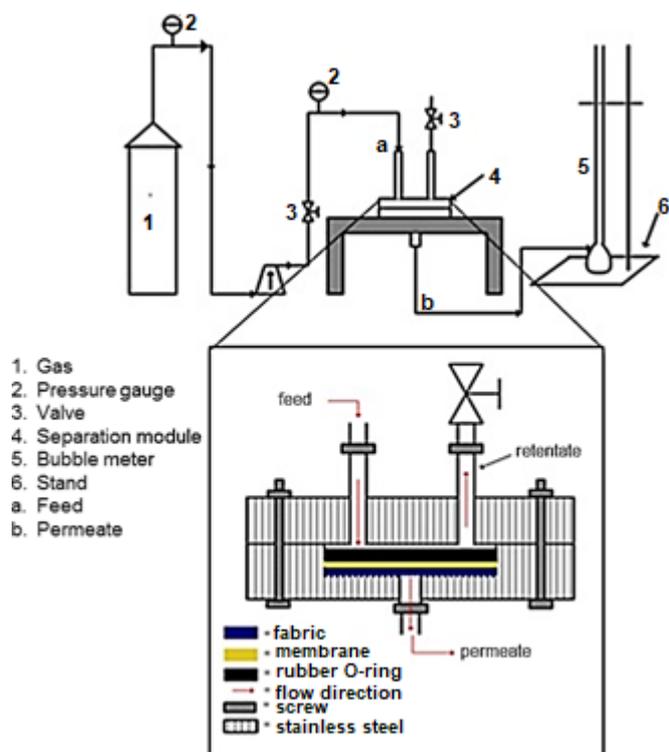


Fig 2. Single gas permeation apparatus

$$P_i = \left(\frac{Q \times l}{\Delta P \times A} \right) \quad (1)$$

where Q is the volumetric gas flow rate at standard temperature and pressure (cm^3 (STP)/s), l is the membrane selective layer thickness (cm), Δp is the differential pressure between feed and system (cmHg), A is an effective surface area of membrane (cm^2).

The ideal selectivity of the membrane was calculated using Equation 2.

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (2)$$

The single gas test apparatus scheme is shown in Fig. 2.

■ RESULTS AND DISCUSSION

Fillers Synthesis

XRD result

The XRD pattern of synthesized zeolite-Y was compared with the diffractogram pattern of ZCC to confirm the alteration in zeolite structure during the pyrolysis process as well as the impregnation process as can be seen in Fig. 3. Both diffractogram in Fig. 3 showing

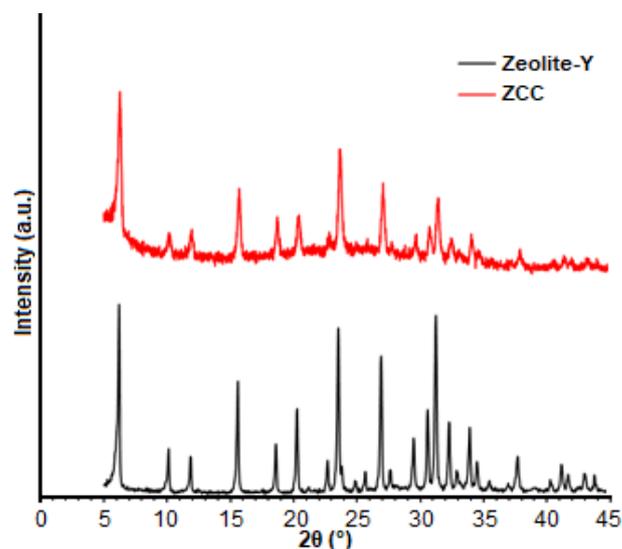


Fig 3. Diffractogram pattern of zeolite-Y (-) and ZTC composite zeolite (-)

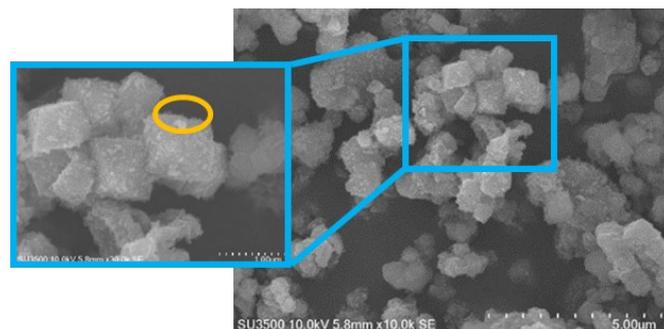


Fig 4. SEM image of ZCC

the same pattern indicating that zeolite was remained unchanged during the sucrose impregnation and pyrolysis at 800°C .

SEM result

The SEM image of ZCC is shown in Fig. 4. The morphology of ZCC filler has the octahedral structure, the same structure as zeolite-Y. This indicating that the structure of template remains unchanged after the pyrolysis and impregnation of sucrose as observed in the diffractogram data. The jagged surface as marked in circle corresponds to the carbon layer that unsuccessfully penetrates through the pore of zeolite. The average particle size of ZCC was 450 nm.

N_2 Isotherm adsorption-desorption

The porosity of a filler used in mixed matrix membrane is an important factor to determine the

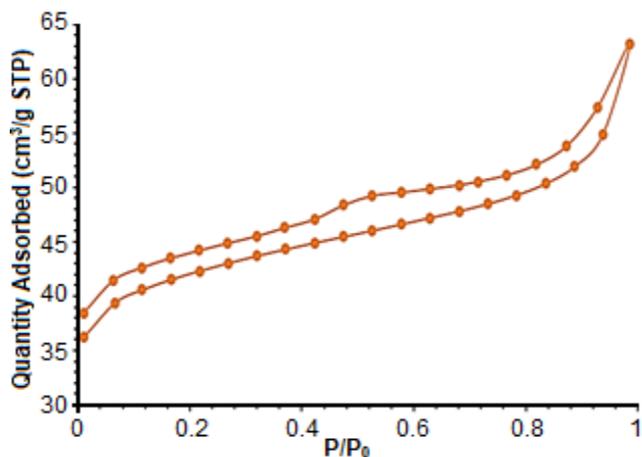
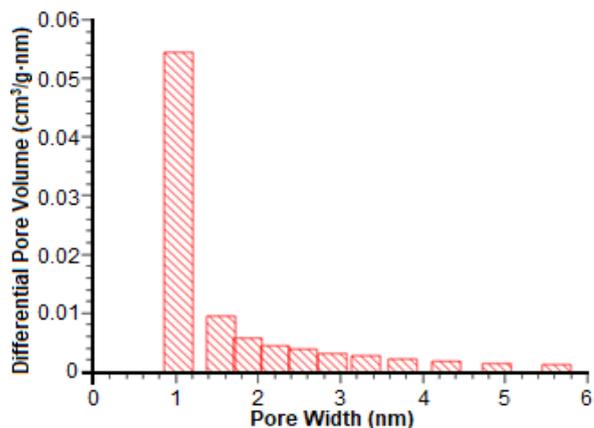
Fig 5. N₂ isotherm of ZCC

Fig 6. Pore size distribution of ZCC, estimated from NLDFT

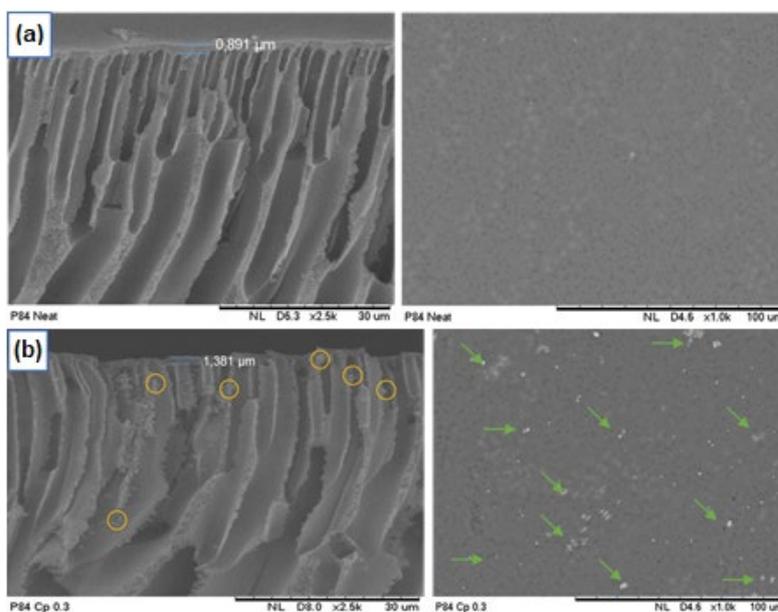


Fig 7. SEM image of (a) pure P84, cross-section (left) and surface (right) and (b) P84/ZCC mixed matrix membrane, cross-section (left) and surface (right)

membrane performance. Fig. 5 shows the N₂ adsorption-desorption isotherm graph of ZCC. The graph showing typical Type I adsorption. The hysteresis was corresponding to the capillary condensation taking place in mesopores. The ZCC has BET surface area of 133.29 m²/g in which contains micropores site the most, up to 72.02%. This micropore facilitated the molecular sieving mechanism in the membrane. The pore size distribution of ZCC was estimated using nonlocal density functional theory (NLDFT) by assuming cylinder pore. The plot pore width against differential pore volume obtained from the N₂

adsorption-desorption data gave the NLDFT graph. As can be seen in Fig. 6, ZCC contains pore in the range 1–6 nm. The average pore size was 1.032 nm, which is in the range of micropore. The mesoporous pore was from the surface carbon layer that did not penetrate through the pore of zeolite.

Mixed Matrix Membrane

SEM result

The morphology of the membrane was characterized using SEM. The cross-section and the membrane surface morphology are shown in Fig. 7. The

cross-section of both membranes consists of a thin dense layer on the top of the membrane and macrovoid on the bottom. The dense layer plays the main role as a selective layer, which will actively filter the fraction of gas that allowed to pass through the membrane and which is not. This layer is formed during the inversion phase process. The selective layer of the membrane has different thickness. The selective layer of the P84/ZCC membrane was 1.381 μm , which is thicker compared to the pristine membrane, which was 0.891 μm . This is due to the incorporation of ZCC on the membrane surface. On the other hand, the macrovoid was formed due to the increment of solvent on low polymeric phase during the inversion phase. The increment of solvent concentration leads to delayed demixing phenomena. Delayed demixing lead to the stability of polymeric solution around the nucleus, making no new nucleus formed in the low concentrated polymer solution. This result in the swelling of the current nucleus for macrovoid [24]. The macrovoid structure could be finger-like or sponge-like structure. The sponge-like structure is formed when the solvent to non-solvent exchange happen in a short period of time [25].

As can be seen in Fig. 7(a), the surface of the pure

P84 was smooth. On the other hand, the P84/ZCC mixed matrix membrane surface showed a white spot, pointed by the green arrow, which corresponds to the ZCC filler. The filler is well dispersed on the membrane surface. Having the well-dispersed filler in mixed matrix membrane is important as it would enhance the performance of the membrane in any spot of the membrane surface. Furthermore, it would hinder the formation of a void on the membrane surface, which leads to the membrane fails.

AFM result

The membrane topography was characterized using AFM and shown in Fig. 8. Yellow color on the 2D image indicating the peak on the surface, meanwhile the darker color indicating valley or pore. The pristine membrane has a smoother surface compared to the mixed matrix membrane. The roughness of the mixed matrix membrane was due to the presence of ZCC filler. The result shows good agreement to the SEM image.

The surface roughness of the membrane increased with the presence of ZCC filler. The Ra value of pristine membrane was lower compared to the membrane with ZCC filler, which was 0.215 to 0.586 μm , respectively.

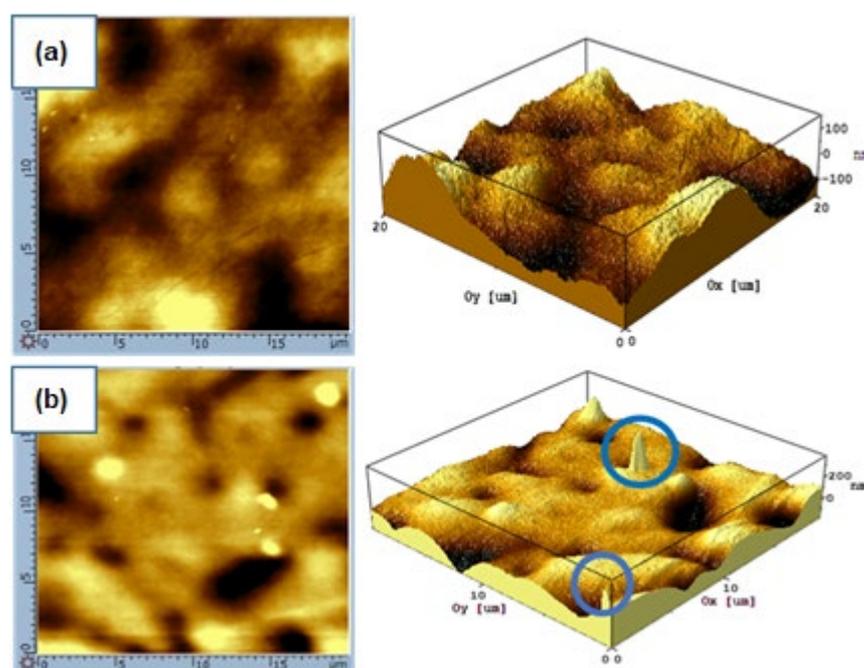


Fig 8. The AFM image of (a) pristine membrane and (b) P84/ZCC membrane

This was due to the filler spread along the membrane surface. This is the typical result of a mixed matrix membrane and was also observed previously [26]. Moreover, on the 3D image of the P84/ZCC membrane, there was a peak with the height about 200 nm, marked with a blue circle. This peak corresponds to the ZCC filler and indicating that half of the filler body was incorporated on the membrane surface. This indicates that the filler is well installed on the membrane surface and avoids the filler to peel-off from the membrane.

TGA

The membrane thermal stability was characterized using TGA. The result is shown in Fig. 9. As can be seen in Fig. 9, all of the membranes experienced three steps of mass loss. The first step was 2% mass loss of the evaporation of water that begins at a temperature of 100 °C. Then followed by 14% mass loss of the evaporation of excess of NMP solvent that not exchanged during the phase inversion in the coagulation bath. The final step was the decomposition of the P84 polymer at 400 °C.

The pristine membrane was started to decompose at a temperature of 400 °C. On the other hand, with the addition of ZCC 0.3%, the initiating decomposition temperature increased to 415 °C. This indicated that the thermal stability of the membrane improved in the presence of ZCC filler. Good thermal properties of ZCC, like any other carbon material, make the membrane more thermal resistance by adsorbing the heat during the analysis process. This lead to the slower the rate of polymer decomposition. The same pattern result was also observed previously [27-28]. On contrary, the use of silica nanocomposite did not affect much in the thermal stability [29]. The increase of decomposition temperature

with an addition of ZCC might indicate a fair interfacial interaction between the polymer and ZCC filler [30].

Single gas test result

The gas separation of all prepared membranes was evaluated to CO₂ and CH₄ gas. The permeability and ideal selectivity performance of membrane were listed in Table 1. The membrane permeability for CH₄ gas was increased significantly to 6.03 Barrer, while the CO₂ permeation was improved up to 12.67 Barrer. The permeability was mainly controlled on how well the gas transport through the membrane. The ZCC filler provides pore regularity that makes the gas travel at ease inside the membrane. Furthermore, the presence of zeolite-Y in the basic form of Na, improve the gas affinity of CO₂ due to the acid-base reaction. Furthermore, by providing a lot of microporous sites, ZCC allowed to selectively separate the gas via molecular sieving mechanism. The diffusion of a smaller gas is much

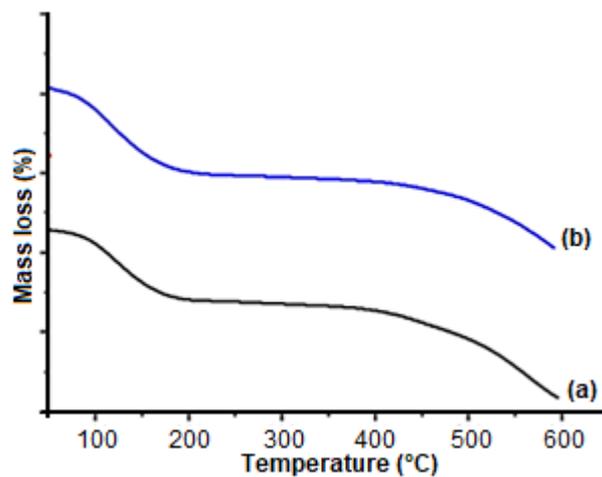


Fig 9. TGA graph of the prepared membrane a) Pristine Membrane and b) P84/ZCC mixed matrix membrane

Table 1. Separation performance of samples studied in this work and comparison with the other result

Samples	CH ₄ (0.38 nm)	CO ₂ (0.33 nm)	Ideal Selectivity CO ₂ /CH ₄	Ref.
	Permeability (Barrer)	Permeability (Barrer)		
Pristine	0.88	0.67	0.76	This work
P84/ZCC 0.3%	6.03	12.67	2.10	This work
Matrimid/Zeolite 4A	4.25	9.36	2.20	[32]
P84/4%SiO ₂	-	0.92	-	[29]
P84 Hollow fiber	3.55	2.70	0.76	[33]

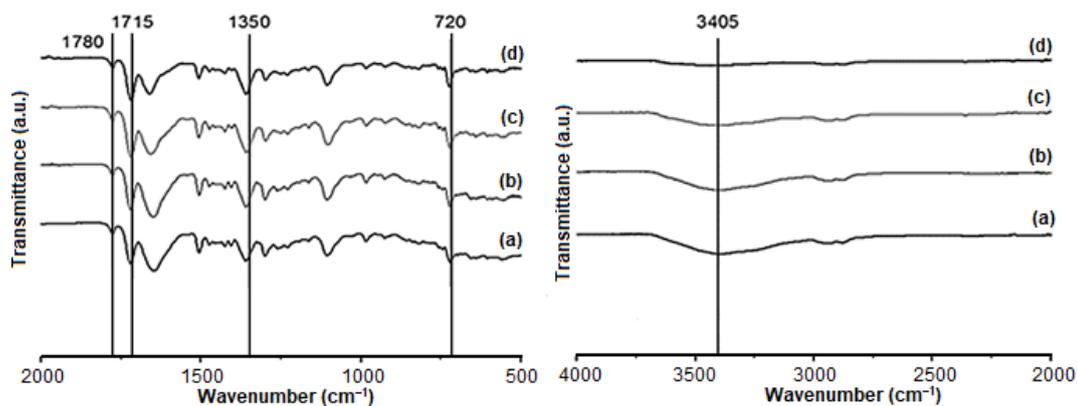


Fig 10. The FTIR spectra of (a) P84 membrane before gas permeation test, (b) P84 membrane after permeation test, (c) P84/ZCC membrane before gas permeation test, and (d) P84/ZCC after gas permeation test

easier compared to the bigger gas. In this case, CO₂ with diameter kinetic of 0.33 nm are able to diffuse faster through the membrane. On the other hand, CH₄ with a diameter of 0.38 nm have slower diffusion.

The selectivity of the membrane also improved significantly by 277% with the addition of ZCC 0.3%. The selectivity of the membrane is mainly controlled by the dense layer of the membrane. The gas transport mechanism usually occurs via solution diffusion on the body of the polymer. However, the gas transport mechanism is able to shift to the molecular sieving mechanism in the presence of microporous inorganic filler such as zeolite or microporous carbon [30]. By having the zeolite and carbon in the structure of ZCC, allowed the membrane to selectively separate the gas molecule in the molecular level.

Furthermore, the FTIR was utilized to observe the mechanism of gas transport in the membrane. The FTIR spectra were shown in Fig. 10. The peak appeared at a wavenumber of 720 cm⁻¹ was coming from C=O bonding, 1780 cm⁻¹ correspond to C=O asymmetric, 1715 cm⁻¹ correspond to C=O symmetric, and 1350 cm⁻¹ was corresponded to C-N [31]. All of those peaks were observed in all membranes and this peak was originated from P84 co-polyimide. Since in this research ZCC loading was low (only 0.3 wt%), the zeolite peak was overlapped with the peak of P84, around 1000-720 cm⁻¹. Furthermore, the C=O peak that coming from CO₂ was not observed in all membrane, indicating that no interaction occurred between the CO₂ and membrane.

The same phenomenon also occurred in the CH₄ case. This indicates that the adsorption did not occur during the permeation test and selectivity was facilitated by solution diffusion and molecular sieving mechanism. The broad peak that appeared at 3750–3000 cm⁻¹ was corresponded to the O-H hydrogen from moisture. As can be seen in the spectra, the intensity of this peak decreased with the addition of ZCC. This result confirms that the coating of carbon in the zeolite pore help to reduce the affinity toward water molecule.

■ CONCLUSION

The addition of microporous inorganic filler of ZCC to the polymeric membrane lead to the improvement in the thermal stability and as well as the separation performance. The filler has fair interfacial interaction with the P84 polymer by improving the thermal stability. Furthermore, ZCC allowed the membrane to perform molecular sieving mechanism during the separation process. The membrane did not create chemical interaction with the permeate gas. Later on, the addition of ZCC reduces the affinity of the membrane toward the water molecule. Overall this was a promising filler for gas separation application as it increased the overall performance of the membrane. It would be benefited more if it applied in the inorganic membrane such as carbon membrane.

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