

Performance of Annealed Composite Cellulose Acetate/NaA Zeolite Membrane in Carbon dioxide/Methane Gas Separation

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Abstract

Ramie (*Boehmeria nivea*) is one type of plant used to produce high quality cellulose fiber. Its fiber is convertible to cellulose acetate (CA), which is commonly used as membrane's material. Dense CA membrane is used in gas permeation process and the performance is improvable by mineral blending and annealing. This study aims to determine the characteristics of modified CA membranes and the performance in separation of CO₂/CH₄ gases. Membrane preparation was carried out by using phase inversion technique, while annealing was carried out at 60°C. Furthermore, NaA zeolite was added with various concentrations, which include 5, 10, 15 and 20%. Gas permeation was carried out at 4 barrer for an hour. The performance of the membrane was measured based on its permeability and selectivity. The results showed that CA membrane with 10% zeolite yielded the best performance with CO₂ and CH₄ permeability of 140.55 and 22.25 barrer respectively and selectivity of CO₂/CH₄ 6.32.

Keyword: Ramie, cellulose acetate membrane, NaA zeolite, annealing, gas permeation.

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1. INTRODUCTION

Ramie's fiber (*Boehmeria nivea*) has a strong fiber compared to cotton due to its long and flexible nature. Furthermore, it contains α -cellulose, hemicellulose, pectin and lignin up to 93%, 2.5%, 0.63% and 0.65%, respectively (Tarmansyah, 2007). The abundance of cellulose's content makes it useful as a source of cellulose. Ramie's cellulose has some advantages, which include being easily isolated with economic way and having good mechanical properties as reinforcement in composite polymer (Liu *et al.*, 2007; Novarini & Sukardan, 2015). The isolated cellulose is commonly converted into cellulose acetate (CA) (Yuniarti, 2008), which is used as membrane's material and is applicable in pervaporation (Ernawati, 2014), brackish water treatment (Supriyadi *et al.*, 2013) and gas permeation (Sanaeepur *et al.*, 2014). Sridhar *et al.* (2014) stated that CA membrane has been

used in CO₂ gas permeation process and the dense form is more desirable compared to the porous form, since it provides better selectivity. However, based on the study by Ernawati (2014), CA membrane has low performance when used as dense membrane in separating materials due to its high swelling degree. In gas separation, the interaction between CA membrane's surface with both carbon dioxide (CO₂) and methane (CH₄) gases is almost same. This is based on their own gas kinetic diameter (3,3 Å for CO₂ and 3,8 Å for CH₄), which are not significantly different. Therefore, both gases are able to diffuse through the CA membrane.

For the case of molecular mobility, CA membrane should be made asymmetrically, which significantly changes its surface morphology in order to obtain higher gas production. This process is referred to as membrane modification. Many researchers

have modified CA membrane to improve its separation ability by mineral addition (Ernawati, 2014), annealing process (Sanaeepur *et al.*, 2014) and substitution of acetyl groups (Yuniarti, 2008). Dogan & Hilmioğlu (2010) blended a polar NaA zeolite to CA membrane in order to improve the polarity of the membrane. Furthermore, Sanaeepur *et al.* (2014) annealed mixed CA-zeolite membrane, which led to the conversion of the membrane's porous structure to a denser state, making it more selective. CA-based membrane is one of many materials that have been used in the permeation of gas mixture separation, due to its stability and low-cost preparation process (Zhou *et al.*, 2011).

Gas permeation is one of many processes for separating mixture of gases due to its high energy efficiency and cost, simplicity and no phase conversion (Baker, 2012). Jeon & Shin (2017) separated CO₂ from a mixture of CO₂/CH₄ using CA membrane via permeation gas process. This separation was carried out based on the polarity difference of the mixture's component. CO₂ is more polar compared to CH₄, therefore, it properly interacted with the surface of the membrane (Nik *et al.*, 2012). Furthermore, carbon dioxide needs to be separated from methane to obtain a better gas quality, because it is corrosive and produces less energy during burning process (Korakianitis *et al.*, 2011).

This study aims to produce a modified CA membrane by mineral addition (NaA zeolite) and annealing, which is to be applied in the permeation of CO₂/CH₄ gases mixture. Furthermore, to determine the characteristics of the membrane and its performance in the separation of CO₂/CH₄ gases.

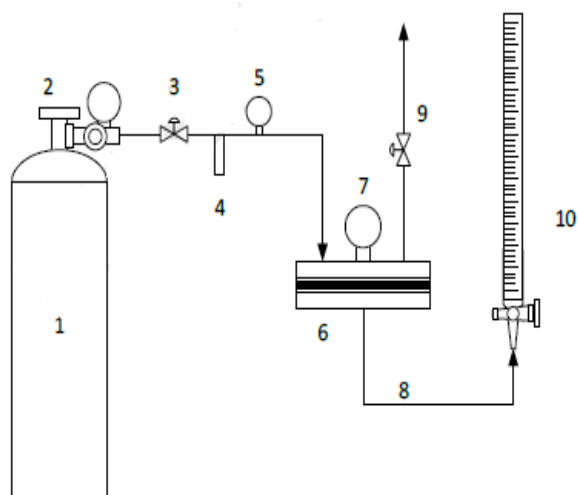
2. MATERIALS AND METHOD

Material and Apparatus

The apparatus used in this study include glass laboratory apparatus, buchner funnel, desiccator, oven, magnetic stirrer, glass plate, gas permeation apparatus, fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM) and universal testing machine (UTM).

Furthermore, materials used in this study include: Ramie cellulose from Microbiology Laboratory, Padjadjaran University, acetic anhydride (C₄H₆O₃) (Merck), distilled water (H₂O), glacial acetic acid (CH₃COOH) (Merck), hydrochloric acid

(HCl) (Merck), sulfuric acid (H₂SO₄) (Merck), oxalic acid (C₂H₂O₄) (Merck), methylene chloride (CH₂Cl₂) (Merck), ethanol (C₂H₅OH) (Merck), CO₂ and CH₄ gases (Sangkuriang), phenolphthalein indicator (C₂₀H₁₄O₄) (Merck), sodium hydroxide (NaOH) (Merck) and NaA zeolite (Wiko No. 267-00595).



1. Gas container (CO₂ and CH₄)
2. Gas valve
3. Controller valve
4. Flowmeter
5. Barometer
6. Membrane's module
7. Barometer
8. Permeate flow
9. Pressure controller valve
10. Bubble flowmeter

Figure 1. Permeation gas apparatus (Tutuk *et al.*, 2018)

Cellulose Acetylation

Ramie's cellulose (10g) was added to 250mL acetic acid glacial and stirred using a magnetic stirrer for 30minutes. Afterwards, 1.6mL of sulfuric acid and 97mL acetic acid glacial were added to the mixture and stirred for 25minutes. Acetic anhydride (100mL) was further added to the mixture and stirred for 30minutes, after which the mixture stood for 14hours at room temperature. The mixture was placed into the stirred distilled water until it precipitated and further vacuum filtered to remove its solvent and water. The CA residue was washed with distilled water and dried at 70°C for 24hours (Kusumawati & Nurhayati, 2014).

Determination of Acetylation Degree

The Acetylation degree of cellulose acetate was determined by placing 0.1g CA inside an erlenmeyer flask and adding 5mL sodium hydroxide 0.25M and 5mL ethanol. This mixture was left to stand for 24hours. Afterwards, 10mL hydrochloric acid 0.25M was added to the system and left to stand for 30 minutes. Next, the mixture was titrated with a standard solution of sodium hydroxide 0.25M using phenolphthalein as an indicator. The Acetylation degree was determined by the equation (Filho *et al.*, 2008):

$$AD (\%) = \frac{[(Vb_i + Vb_t)\mu_b - V_a \cdot \mu_a]43.100}{m_{ca}}$$

Where AD is acetylation degree, Vb_i is volume of sodium hydroxide added to the system (mL), Vb_t is volume of sodium hydroxide spent in titration (mL), μ_b is concentration of sodium hydroxide (N), V_a is volume of hydrochloric acid added to the system (mL), μ_a is concentration of hydrochloric acid (N), 43 is molar weight of acetyl group (g/mole) and m_{ca} = weight of CA sample (g).

Annealed Composite CA/NaA Membrane's Preparation

CA powder 10% w/w of total mass of solution was dissolved in methylene chloride until homogeneous. Afterwards, various percentage (of CA weight) of NaA zeolite was added gradually to the mixture and stirred for 24h. The mixture was placed in refrigerator for 24h and later casted in a glass plate. Furthermore, the membrane at glass plate was placed in desiccator for 24h (Ernawati, 2014). For the annealing process, the formed composite membrane was placed in oven at 60°C for 30minutes. Afterwards, it was replaced in a desiccator for 24h (Supriyadi *et al.*, 2013).

Gas Permeation

The membrane was roundly cut with 5.56cm diameter, which is the effective area for separation and placed in membrane's module (Figure 1, point 6). It was further treated by the 4 bar of pure CO₂ and CH₄ gases. Afterwards, pure CO₂ and CH₄ gases were flown to gas permeation apparatus for 5minutes with the valve closed at module connector. This was to ensure that the adaptive condition for membrane is maintained. Next,

the valve at module connector was opened and then the volume of gas passing through bubble flow was observed with interval from 0 till 3600 seconds. The volume of gas that passed through was recorded and the data was plotted to V/AP_1 (V = gas volume in permeate/cm³, A = membrane area/mm², P_1 = feed pressure/cm Hg) versus time graph.

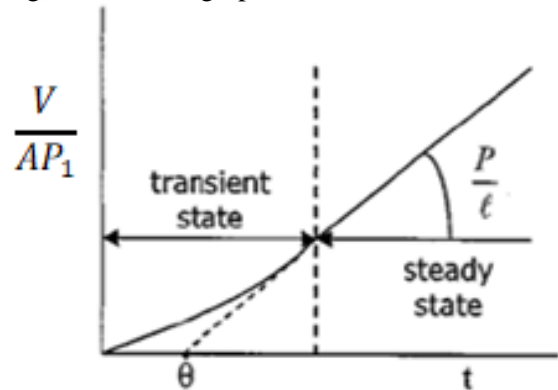


Figure 2. Permeation's steady state determination

The straight line indicates the curve's gradient which is shown by P/l value. This value was further used to determine the pure CO₂ and CH₄ gases permeation, using the following equation:

$$P = l \times \text{curve's gradient}$$

Next, the selectivity was obtained using the following equation:

$$\alpha = \frac{P_{CO_2}}{P_{CH_4}}$$

where P = Membrane's permeability (Barrer), l = membrane's thickness (mm) and α = membrane's selectivity

Membrane's Characterization

The membranes produced were characterized for the following characteristics: functional groups, morphology and mechanical strength using Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Universal Testing Machine (UTM) instruments, respectively.

3. RESULT AND DISCUSSION

The value of acetyl degree of synthesized CA was 41.61% and it was classified as cellulose diacetate (Gaol *et al.*, 2013). This CA formation was confirmed from its functional group using FTIR, by comparing its functional group to commercial CA. FTIR spectra of CA is showed in figure 3.

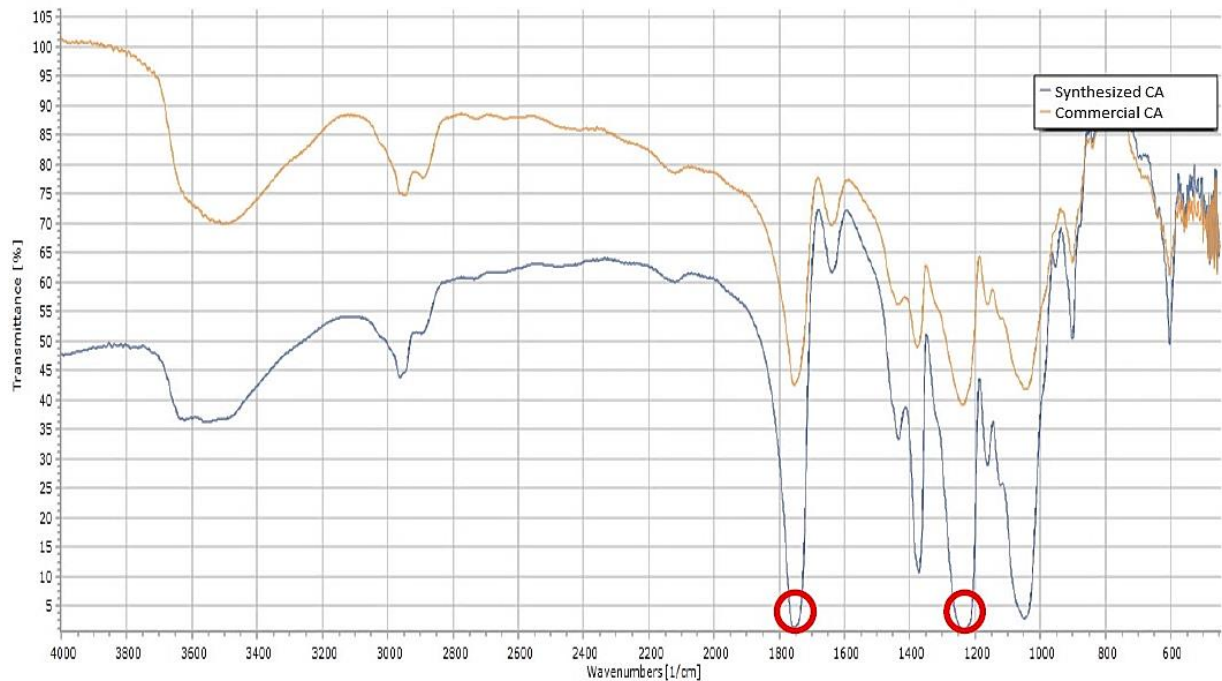


Figure 3. FTIR spectra of commercial (orange) and synthesized CA (blue).

From figure 3, it is seen that both the synthesized and commercial CA showed an absorption range for hydroxyl group of 3400 cm^{-1} . Furthermore, both spectra showed absorption of carbonyl (C=O) and ester (C-O) group as acetyl group compiler, around 1750 and 1230 cm^{-1} area, respectively. Therefore, with this functional group data, CA was successfully synthesized.

The composition of CA/NaA membrane were 10% CA (w/w), 90% (w/w) methylene chloride (as solvent) and various amount (5 – 20 %) (w/w of CA weight) of NaA zeolite. Based on Ernawati (2014), CA membrane filled with 10% of zeolite shows good separation performances. The stirring process during its synthesis may cause bubbles to be trapped in the membrane's matrices, which are capable of inhibiting its homogeneity. This may also lead to the formation of void or free volume inside the membrane, which is capable of influencing its thickness and mechanical strength. Therefore, membrane's solution was placed in refrigerator for 24h to throw off the bubbles and inhibit the evaporation of solvent (Ernawati, 2014). Furthermore, membrane's casting was carried out using the phase inversion technique, which involves changing the liquid phase of polymer into its solid phase under controlled condition

(room temperature) (Mulder, 1996). Annealing of membranes were carried out at 60°C based in the study by (Supriyadi *et al.*, 2013), which stated that at this temperature, higher compactness is attainable. From the membrane's morphology, it was seen that agglomerations of NaA zeolite were formed at CA/NaA membrane's surface (Figure 4b). This was clearly different from the CA membrane's surface (Figure 4a).

SEM micrograph of CA, CA/NaA and annealed CA/NaA membrane's cross section are shown in Figure 5. CA/NaA membrane's thickness with and without annealing showed no difference at $24.6\text{ }\mu\text{m}$. Furthermore, in CA/NaA membrane there was a crack and NaA zeolite agglomerate were formed, while in the annealed membrane both the crack and agglomerate were reduced. Sanaeepur *et al.* (2014) stated that the morphology of zeolite filled membrane was different from CA membrane because there was a rearrangement of polymer chain molecules with zeolite which affected the CA-zeolite interaction. Meanwhile, annealing led to a better adhesive force between CA polymer and zeolite, therefore the membrane became denser. This same statement was made by Supriyadi *et al.* (2013), stating that the effect of annealing on CA membrane led to the rearrangement of

membrane's molecules, which made it more stable and improved CA-zeolite interaction.

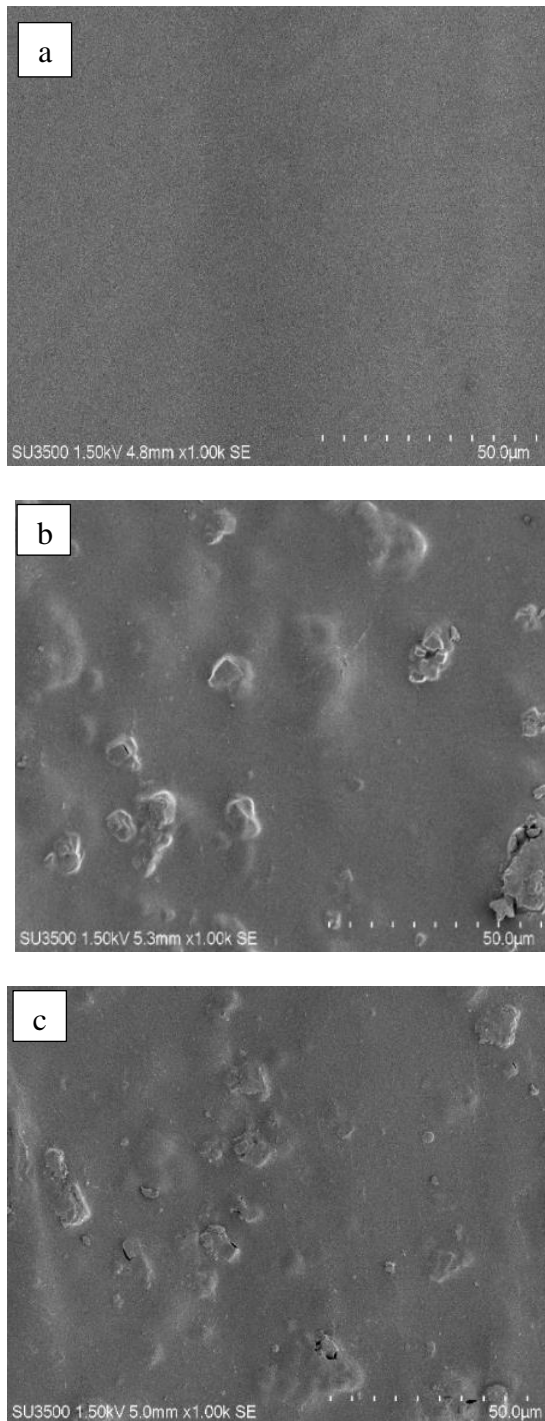


Figure 4. Surface of CA (a), CA/NaA 10% (b), and annealed CA/NaA 10% (c) membranes.

Figure 6 showed the composition of elements in Ca/NaA membrane. Ca/NaA membrane contained sodium, aluminum and silicon, which were obtained from NaA zeolite. The sum of sodium and aluminum had higher mass percentage compared to silicon (1.92:0.86),

which made the membrane polar. Furthermore, this showed the precise ratio of NaA zeolite. Sanaeepur *et al.* (2014) stated that the added aluminum and silicon are capable of changing the polarity of the membrane. The addition of NaA zeolite enhanced the polymer physical properties of CA as a reinforcement agent, which made them a composite material. Furthermore, NaA zeolite bond physically to CA polymer, therefore, there was no structural change of both substances.

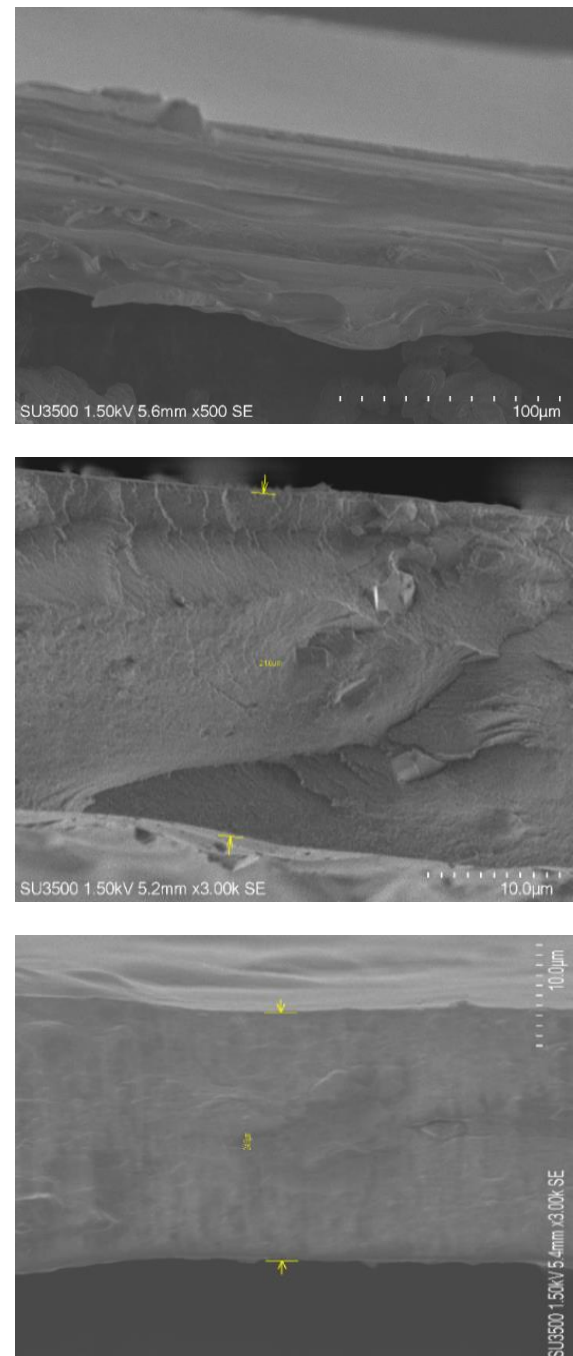


Figure 5. Cross section of CA (a), CA/NaA 10% (b), and annealed CA/NaA 10% (c) membranes.

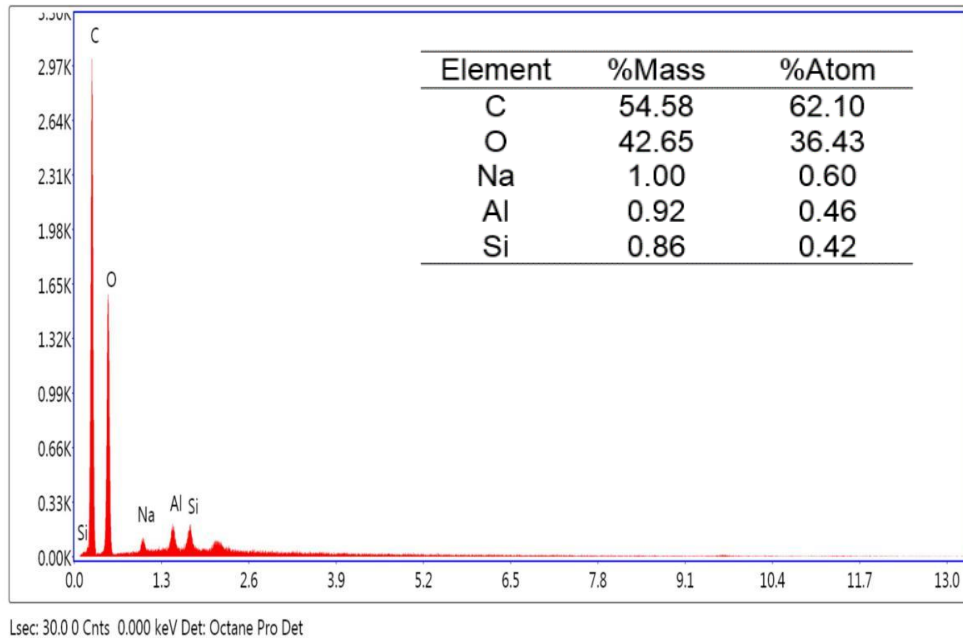


Figure 6. EDX analysis of CA/NaA 10% membrane’s surface.

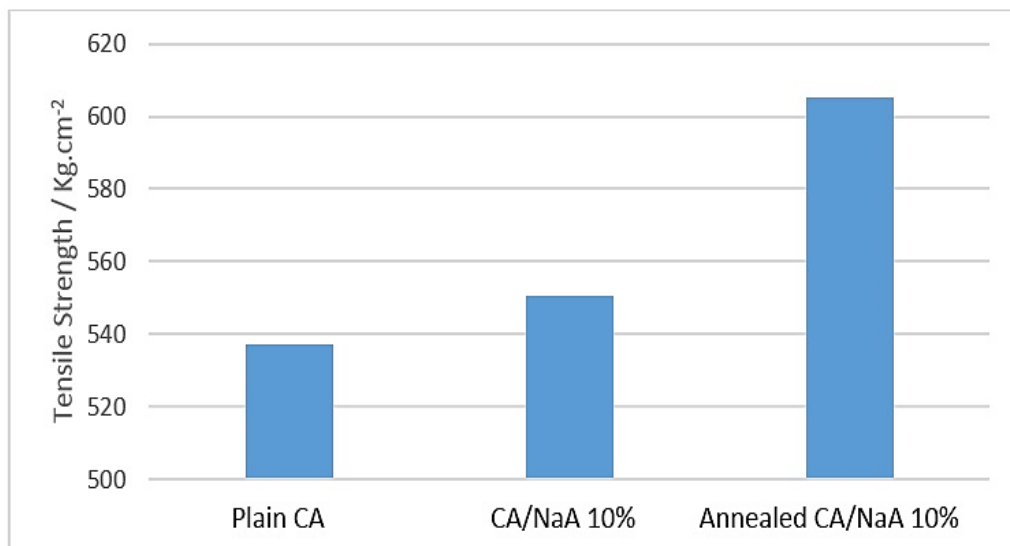


Figure 7. Tensile strength analysis of CA, CA/NaA 10%, and annealed CA/NaA 10% membrane.

The Membranes tensile strength are showed in Figure 7. Plain CA membrane without zeolite nor annealing process showed TS value of 537.07kg/cm². Meanwhile, the addition of NaA zeolite to CA membrane showed an improvement in TS value to 550.54kg/cm². Furthermore, the annealed composite CA/NaA membrane showed higher TS value of 605.26kg/cm².

From figure 7, it is seen that the addition of NaA zeolite improved the TS value. This was because NaA zeolite particles interacted physically with CA polymer matrices and influenced its physical properties (Sanaeepur et

al., 2014). The presence of sodium and aluminum metals as well as silicon, a semimetal improved tensile strength by filling its matrices (Arefi et al., 2016). Furthermore, annealing improved the adhesive interaction of CA polymer and NaA zeolite, therefore the density of membrane increased and also improved its TS improvement by 605.26kg/cm². In addition, it led to the rearrangement of CA polymer, resulting in a more compact membrane (Figure 5c), therefore, with its high density, the TS value also increased (Sanaeepur et al., 2014; Supriyadi et al., 2013).

The addition of zeolite with and without annealing at 60°C, which influenced membrane permeability in CO₂ gas is shown in Figure 8. It is seen that CO₂ gas permeability of CA/NaA membrane increased along with the addition of NaA zeolite from 5% to 15%, with permeability value of 88.2 until 106.65 barrer, but decreased with 20% of NaA zeolite to 101.1 barrer. This was due to the NaA zeolite porous wall, which had a high selectivity to CO₂ gas. This selectivity occurred because of its quadrupole moment which led to polar surface interaction (Dorosti *et al.*, 2015). Furthermore, when the amount of zeolite increased to 20%, its permeation decreased. This was because of the less adhesive interaction between zeolite and CA polymer, due to saturated state (Sanaeepur *et al.*, 2014).

Annealed CA/NaA membrane showed high permeability with 5% and 10% zeolite content, with values of 98.25 and 140.55 barrer, respectively. All annealed membrane had higher permeability compared to non-annealed. This was due to the heat energy that broke the intermolecular hydrogen bond, which led to an increase in the polymer chain shift, accompanied by the formation of intramolecular hydrogen bond. Consequently, this causes the membrane to become denser, more selective to CO₂ gas and diffusion becomes easy (Sanaeepur *et al.*, 2014). Decrease in permeability occurred with the addition of 15% and 20% NaA zeolite, with values of 120.75 and 115.8 barrer, respectively. This was due to the higher zeolite

amount, which affected several CA polymer trapped in NaA zeolite pores. Therefore, it was difficult for CO₂ gas to diffuse through the membrane (Sanaeepur *et al.*, 2014).

Figure 9 shows the membrane's permeability to CH₄ gas. It is seen that the permeability of CA/NaA decreased along with the addition of NaA zeolite. The lowest permeability i.e. 77.55 barrer was seen at 20% NaA zeolite. Furthermore, the annealed CA/NaA membrane showed permeability improvement along with the addition of 10 to 20 % NA zeolite, with values of 22.5 to 68.25 barrer. From the SEM micrograph, it was seen that the presence of NaA zeolite agglomerate decreased the density of its pores. Meanwhile, the presence of free volume in polymer matrices allowed the CH₄ gas to diffuse through the membrane (Dorosti *et al.*, 2015; Sanaeepur *et al.*, 2014).

CA/NaA membrane's had lower CH₄ permeability compared to CO₂ gas, due to the properties of CH₄, which are less polar than CO₂, therefore it interacted weakly with the membrane's surface which is polar (Arefi *et al.*, 2016). Furthermore, the kinetic gas diameter of CH₄ (3,8 Å) was larger compared to that of CO₂ gas (3,3 Å), which led to difficulty in diffusing through the membrane's surface (Dorosti *et al.*, 2015; Sridhar *et al.*, 2014). Annealed CA/NaA membrane had lower permeability because of its denser morphology and higher interaction between CA polymer and NaA zeolite (Sanaeepur *et al.*, 2014).

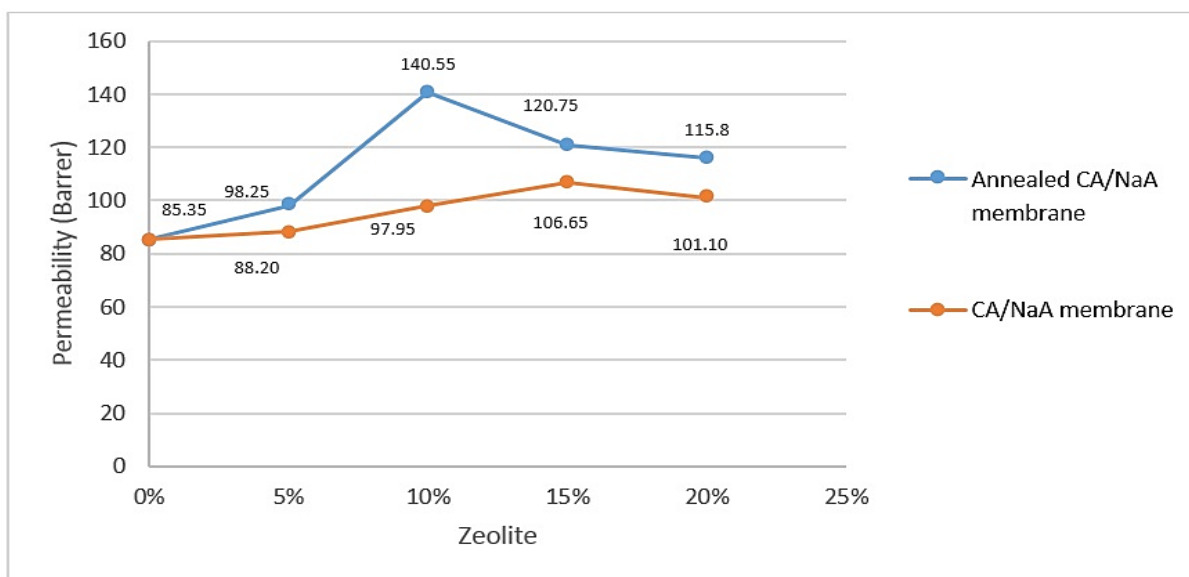


Figure 8. CO₂ permeability at 4 bar

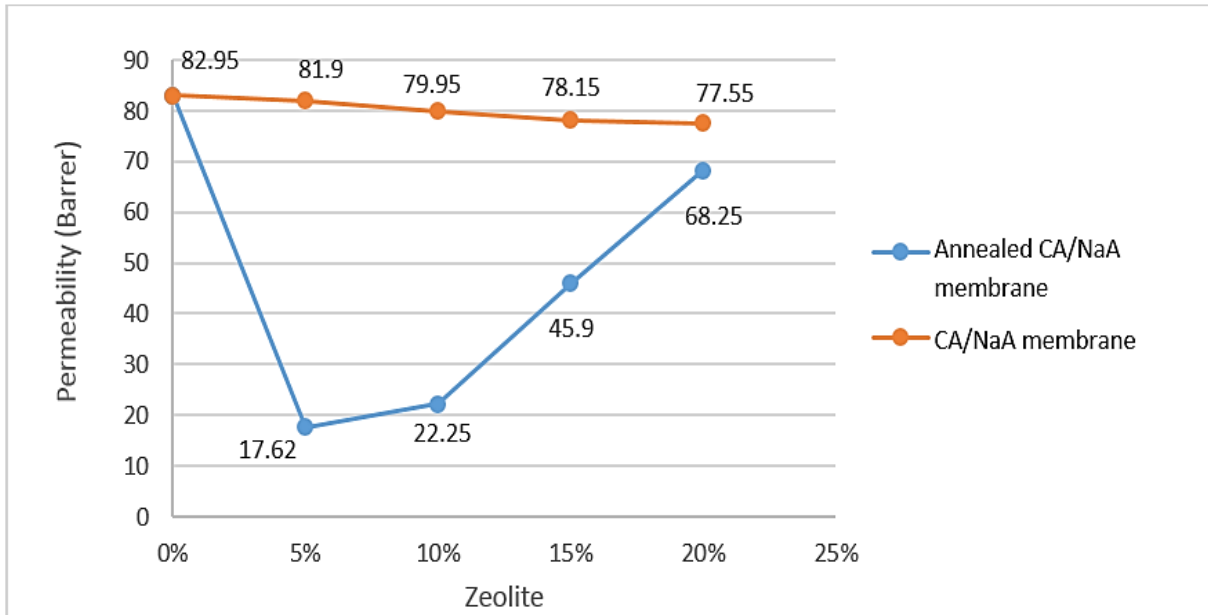


Figure 9. CH₄ permeability at 4 Bar

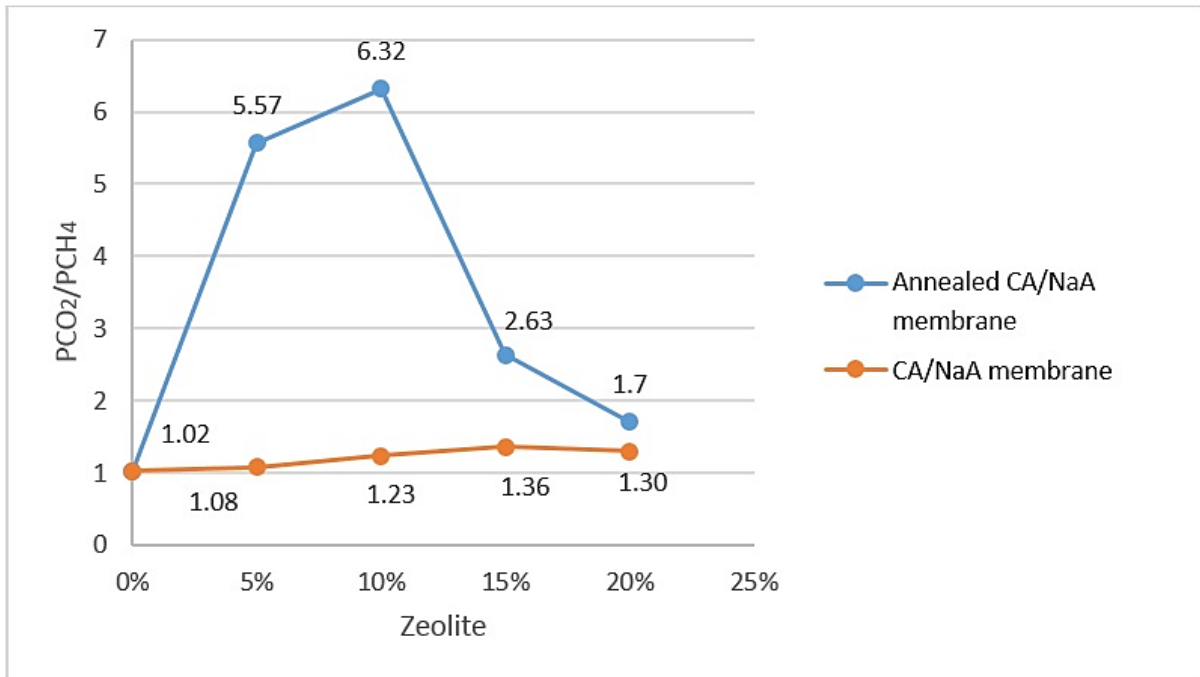


Figure 10. Membrane selectivity in Separation CO₂/CH₄ gases mixture at 4 Bar

Figure 10 shows the difference in membrane selectivity of CO₂/CH₄ gases mixture between CA/NaA and annealed one. It is seen that the CA/NaA membrane filled with 15% NaA zeolite had the highest selectivity value of 1.36, while 20% NaA zeolite showed a decreased value to 1.30. The annealed CA/NaA membrane had the highest selectivity value of 6.32 with 10% NaA zeolite, which decreased with the addition of more zeolite. The increase in the selectivity value for

CO₂/CH₄ gases was due to the ability of NaA zeolite to adsorb CO₂ at its porous wall. CO₂ gas diffused easier compared to CH₄ through zeolite's porous channel, because it had higher polarizability and quadrupole moment. Furthermore, sodium ion (Na⁺) from the NaA zeolite's porous produced a fair electrostatic interaction to CO₂ gas (Jusoh *et al.*, 2017; Sanaeepur *et al.*, 2014). Meanwhile, the decreased selectivity could be caused by zeolite agglomerate, which decreased the

mobility of CO₂ through polymer chain and also leading to lower diffusion and selectivity. Therefore, the presence of non-selective membrane's free volume made the diffusion of CH₄ easier (Nik *et al.*, 2012).

4. CONCLUSION

From the results obtained, it was concluded that 10% annealed CA/NaA membrane was the best composition on CO₂/CH₄ gases mixture separation based on its characteristics and performances in gas permeation. Its permeability to CO₂ and CH₄ gas were 140.55 and 22.25 barrer, respectively, with 6.32 selectivity value.

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