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Blend Cellulose Acetate/Multi-Walled Carbon Nanotubes Mixed Matrix Membrane for CO₂/N₂ Separation

Nigel Wei Ming Chin^a, Zeinab Abbas Jawad^{a*}, Bridgid Lai Fui Chin^a, Peng Chee Tan^b^aDepartment of Chemical Engineering, Faculty of Engineering and Science, Curtin University Malaysia, CDT 250, 98009 Miri, Sarawak, Malaysia^b School of Energy and Chemical Engineering, Xiamen University Malaysia, Jalan Sunsuria, Bandar Sunsuria, 43900 Sepang, Selangor Darul Ehsan, Malaysia

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ABSTRACT

The carbon dioxide (CO₂) in the atmosphere has been increasing extensively over the past decades, which is a major contributor to the global warming phenomenon. Therefore, a highly performing and high cost efficiency membrane technology was proposed to selectively separate the hazardous CO₂. Hence, a Mixed Matrix Membrane (MMM) was incorporated for CO₂/N₂ separation with prospects to surpass the numerous shortcomings of conventional membranes. Thus, this study utilized cellulose acetate (CA) with acetyl content of 39 wt% and 56 wt% blended with multi-walled carbon nanotubes (MWCNTs) to fabricate the MMMs. The gas permeation results had showed that MMMs with functionalized MWCNTs (MWCNTs-F) had demonstrated enhanced separation properties of CO₂/N₂ with a selectivity of 3.084 + 0.019 in comparison to pristine MWCNTs and blend CA-membrane. Hence, the loadings of MWCNTs-F towards the separation performances of the MMMs were then investigated. The CO₂/N₂ selectivity from the gas permeation results showed an increased to 3.72 + 0.014 with optimal loadings of 0.20 wt% of MWCNTs-F within the polymer matrix. The superior performance of the MMM was attributed to the additional developments in the overall sufficient free volumes between the polymer chains. Eventually, the MMM showed insight towards the industrial applications in the gas separation field.

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1. Introduction

The rapid economic development throughout the world has led to an increase in CO₂ emissions worldwide (Mardani et al. 2019). Carbon Dioxide, (CO₂) emissions are mainly due to the burning of coal, deforestation, and petrol which are classified as human-induced warming activities (Sanglimsuwan 2011). CO₂ is one of the Green House Gases (GHGs) that contributes to global environmental problem and the phenomena of global warming of about 58.8%. Annual GHG_s emissions have been recorded and shown to increase at an alarming rate of 85% i.e., from 27Gt to 49Gt (Gigatonnes) from 1970 to the end of 2010 (Sangeetha and Amudha 2018). To mitigate the increasing amount of CO₂ released into the atmosphere, Carbon Capture and Sequestration (CCS) was implemented (Allinson et al. 2017).

In general, absorption, cryogenic, and membrane remains one of the separation options for post combustion capture (Songolzadeh et al. 2014). Based on a study conducted by Barker et al. (2009) on a cement production factory in Scotland, UK, membrane technology was able to offer a high Carbon Capture Rate (CCR) of 85% with 0.62Mt_{CO₂}/year from total carbon emission of 0.72Mt_{CO₂}/year. Membrane technology is an alternative choice to replace the other technologies due to its unique ability to reduce operating costs as energy-driven forces are not required. Furthermore, it has high selectivity properties against the target gas (Powell

and Qiao 2006). Polymeric membranes were the first commercial feasible approach in membrane technology for gas separation due to its distinct physical and chemical properties in handling large amount of feeds (George et al. 2016).

However, the performance of these membranes are governed by their limited separation ability (selection factor increases, permeability decreases and vice versa) (Powell and Qiao 2006). Thus, alternative types of membranes have been developed to overcome these limitations. This has led to the development of inorganic membranes which possess superior separation performance and absolute chemical stability properties in harsh environmental conditions as compared to the polymeric membranes (Belaissaoui and Favre 2014). However, the limitations of the inorganic membranes are their exceptionally high fabrication, which are subjected to various handling issues (eg. high susceptibility to brittleness) (Caro et al. 2000). Thus, a new approach was taken towards the development of the membrane to provide a low cost option and to surpass the upper-boundary limit between selectivity and permeability (Chung et al. 2007). In order to overcome the shortcomings of polymeric and inorganic membranes and optimize separation performance, a Mixed Matrix Membrane (MMM) which consisted of blend Cellulose Acetate (CA) polymer and Multi-Walled Carbon Nanotubes (MWCNTs) was synthesized. These types of membranes are combined and demonstrate

* Corresponding Author: : zeinab.aj@curtin.edu.my

the desired mechanical properties of the polymeric membrane and the high selectivity of the inorganic filler (Chung et al. 2007). In a different study, Ismail et al. (2011) prepared polyethersulfone with embedded MWCNTs and discovered that the highest selectivity was attained at 0.5 wt%. Unfortunately, the formation of microvoids became prominent causing the gas selectivity to decrease when 1-3 wt% of MWCNTs loadings were incorporated (Ismail et al. 2011).

Therefore, the aim of this work is to fabricate a highly performed and efficient MMM and optimized MWCNT loadings for a superior gas separation performance. Up to date, no studies have been conducted on the effects of MWCNT loadings when fabricated with a high performing blend CA membrane with acetyl content of 39 wt% and 56 wt% for CO₂/N₂ separation. The blend of high and low acetyl concentrations was used to produce a defect-free smooth membrane from the strong interaction amongst the polar functional groups and non-polar CO₂ gas. Furthermore, the average acetyl content derived from the blend also enhanced the overall permeance rate of CO₂ gas.

2 Materials and Methods

2.1 Chemicals and Reagents

The CA (acetyl content of 39% and 56%) was obtained from Sinopharm Chemical Reagent Co.Ltd. China. The MWCNTs were acquired from Shenzhen Nanotech of 95 % purity with average inner and outer diameter estimated to be 8.85nm and 26.62nm, respectively and mean lengths of 25 µm. The Ethanol-hexane, acetic acid (CH₃COOH) and α-CD, ACS reagents, 98% were purchased from Merck, Malaysia.

2.2 Functionalization of MWCNTs (MWCNTs-F)

The pristine Multi-Walled Carbon Nanotubes (MWCNTs-P) were first stripped of their moisture by drying them in an oven for 24 hours at a temperature of 120°C. Later, the MWCNTs were functionalized by β-CD through Chen's soft-cutting technique. Through this soft-cutting method, which was performed with an agate mortar and pestle, the concentration ratio between MWCNTs-P and βCD was 1:30wt%. At the same time, ethanol was poured slowly into the mixture to obtain a grayish and high viscosity mixture in the first 10 minutes and after that underwent continuous stirring for another 2.5 hours. At the end of the stirring, a fine gray powder was obtained. Thereafter, the fine gray powder was subjected to heating overnight at a temperature of 80°C (Latif Ahmad et al. 2013).

2.2.1 Preparation of CA Membrane

The membranes were synthesized using the wet-phase inversion technique. The solvent mixture (4 wt% of 39% concentration content CA, 6 wt% of 56% concentration content CA, 63 wt% of CH₃COOH and 27 wt% of deionized water) was subjected to continuous stirring for a period of 3 hours at a temperature of 55°C. Once the CA was completely dissolved, the solution was then cooled to standard room temperature (27°C). Later on, it was subjected to another stirring for 12 hours. After that, the solution underwent ultrasonic degassing to remove any trapped gas bubbles. Thereafter, casting was done at ambient room temperature (27 °C) with an adjusted thickness of 250 µm through an automatic film applicator. Prior to that, the sample membrane was immersed into deionized water bath for a duration of 5 minutes. Subsequently, the membrane sample was transferred into another water bath overnight to eliminate any

left-over solvent. The membrane was then moved into an ethanol bath for a period of 4 hours and later transferred to an n-hexane bath for 1 hour for membrane drying. Lastly, the membrane was then placed between two glass plates for 24 hours to further remove any remaining solvents and stored prior to use (Ahmad et al. 2014).

2.2.2 Fabrication of MMM (CA-MWCNTs)

A solution mixture containing a specific amount of composition of the solid base (MWCNTs-P or MWCNTs-F) and solvent mixture (CH₃COOH and deionized water) was subjected to sonication for 20 minutes. Subsequently, the mixture was stirred continuously for a duration of 4 hours to ensure homogenized particle distribution in the mixture. After that, the CA (4 wt% of 39% concentration content CA and 6 wt% of 56% concentration content CA) was added gradually into the mixture and stirred for 3 hours at a temperature of 55 °C until solid deposits were completely dissolved (Ahmad et al. 2014). The fabrication method of the MMM is similar to the previous method as mentioned in Section 2.2.1. The compositions of blend CA-polymer and MMM are tabulated in Table 1.

2.3 Single Gas Permeation Analysis

The single gas separation performance test was conducted in regards to a previous published work by Ahmad et al. (2014).

2.4 Mean Acetyl Concentration Calculation

The membranes were synthesized by two different acetyl concentrations during the polymeric phase, which consisted of 39wt% and 56 wt% at a ratio of 4:6. The mean acetyl concentration of the fabricated membranes was calculated by equation (1) (Ferraz et al. 2000).

$$\text{Average Acetyl Concentration (\%)} = \text{BR}_{39\%} \times \text{AC}_{39\%} + \text{BR}_{56\%} \times \text{AC}_{56\%} \quad (1)$$

Where:

BR=Blending Ratio

AC=Acetyl Concentration

2.5 Characterization of MMMs

2.5.1 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

FTIR is a form of method used to obtain an infrared absorption and emission spectra of a specified sample which are not limited to solid, liquid and gas forms (Lee et al. 2018). For evaluation, Thermo Scientific Fourier Transform Infrared Spectrometer (NICOLET is10, USA) was used to characterize the functionalized MMM (CA/MWCNTs) with a wavelength range from 600 to 4000cm⁻¹. Each specimen was obtained with 32 scans at 45° incident angle with the aid of a diamond crystal (Lee et al. 2018; Ahmad et al. 2014).

2.5.2 Scanning Electron Microscope (SEM)

In the SEM, a fine focused electron beam is channelled towards the material and scans the surface of the sample (Lee et al. 2018). As a result, several electron-sample interactions occurred that led to the generation of various signals, which changed according to the sample surface topography (Omidi et al. 2017). To prepare the membrane samples for

Table 1: CA-M and MMM (CA/MWCNTs) composition

MMM sample description	CA polymer with acetyl content (wt%)	CA polymer with acetyl content (wt%)	Acetic Acid (wt%)	MWCNTs			
				Deionized Water (wt%)	MWCNTs filler (wt%)	Solid Base β-CD (wt%)	Solid Base MWCNTs (wt%)
CA-M	4	6	63.	27	0.00	0.00	0.00
MMM-0.1P	4	6	62.993	26.997	0.01	0.000	0.010
MMM-0.05F	4	6	62.890	26.953	0.050	0.152	0.005
MMM-0.1F	4	6	62.776	26.904	0.100	0.309	0.010
MMM-0.15F	4	6	62.659	26.854	0.150	0.472	0.016
MMM-0.2F	4	6	62.537	26.802	0.200	0.639	0.021
MMM-0.3F	4	6	62.282	26.692	0.300	0.992	0.033

characterization, the samples were first kept in a cryogenic freezer at -80°C for 24 hours to ensure samples were clean and to allow consistent cracking. Then, the membrane samples were fractionated into small pieces with coatings of platinum sputtering. The samples were later subjected to characterization under a SEM (Hitachi TM3000, Tokyo, Japan).

3 Results and Discussion

3.1 Integration of MWCNTs into Blend Membrane

3.1.1 Membrane Physical Morphologies

Figure 1 demonstrates the physical morphologies of the blend CA-M membrane, pristine MMM (MMM-0.1P) and functionalized MMM (MMM-0.1F), respectively. From Figure 1 (a), it was clearly observed that the blend CA-M membrane exhibited a rough surface with a thin dense skin layer. The hydrodynamic instabilities that occurred from the surface tension gradient led to an imperfect demixing mechanism which caused irregularities on the blend CA-M surface (Idris et al. 2017). Hence, the hydrophilic properties of the CA-M polymer chains had increased the overall surface energy thus, causing water to flow at a relatively fast rate towards the membrane during membrane synthesis (Kamal et al. 2014). As a result, this caused an unsmooth dense skin layer from the disarranged CA-M molecules (Kim et al. 2018).

When the CA-polymer was loaded with MWCNTs-P, the aggregated clusters of MWCNTs-P were clearly found on the membrane surface.

The long term dope stability was affected due to the integration of MWCNTs-P into the polymer matrix, thus leading to unhomogenized dispersion of MWCNTs in the solution (Lee et al. 2018; Latif Ahmad et al. 2013). The particles settling rate and the compatibilities of MWCNTs with the remaining components of the dope were the highly dependent factors towards the homogenized dispersion of MWCNTs (Ismail et al. 2011). The incomplete dispersion of MMM-0.1P in the dope solution and insufficient coalescence between the polymer molecules were the contributing factors towards the reason of defect formation (Ismail and Ping Yean 2003). The agglomeration of the MWCNTs-P was mostly due to strong particle-particle interaction compared to the particle-polymer matrix of Van der Waals forces as well as their hydrophobic nature (Sahoo et al. 2010).

In contrast to the MMM-0.1P, when MWCNTs-F was integrated into the CA polymer, the membrane (MMM-0.1F) was distinguished by its fairly smooth and defect-free surface as shown in Figure 1 (e). The superior interaction between the polymer matrix and the MWCNTs-F led to the uniform homogenized polymer-particle distribution within the membrane, which attributed to the alteration of the physical surface morphology between CA-M and MMM-0.1F (Aroon et al. 2010).

The cross-sectional morphologies of membranes are shown in Figure 1 (b, d and f). The thickness of the blend CA-M, MMM-0.1P and MMM-0.1F were approximated to be $7.02 \pm 0.017 \mu\text{m}$, $7.83 \pm 0.012 \mu\text{m}$ and $6.19 \pm 0.029 \mu\text{m}$, respectively. As seen from Figure 1 (b, d and f), MMM-

Figure 1: SEM cross section and surface morphologies of (a and b) of blend CA membrane (CA-M), (c and d) pristine mixed matrix membrane (MMM-0.1P) and (e and f) functionalized mixed matrix membrane (MMM-0.1F). The membranes were fabricated at constant thickness of $250 \mu\text{m}$.

0.1F exhibited a thinner dense layer as compared to the CA polymer and MMM-0.1P. The change in membrane thickness was due to the alteration towards the original CA polymer packing from the integration of nanofillers (MWCNTs) within the polymer matrix (Silva et al. 2017; Wang 1998). The thinner dense skin layer of MMM-0.1F was due to the existence of a relatively shorter permeation pathway in the membrane from the superior synergistic relationship of the functionalized CNTs and the polymer matrix (Sarraz and Ba-Shammakh 2018). Moreover, a thinner membrane exerts a better gas separation performance as it yields lesser flow resistances (Lee et al. 2018).

3.1.2 Membrane Characterization (ATR-FTIR)

The infrared spectrums of blend CA, pristine MMM (0.1P) and functionalized MMM (0.1F) membranes fabricated with 250 μm thickness are compared in Figure 2. The characteristics bands of 3475.23 cm^{-1} attributed to the O-H group (Kamal et al. 2014). The characteristic peak at 2901.42 cm^{-1} indicated the presence of $-\text{CH}_2$ group (CH stretching) (Pielesz and Biniace 2010). High absorption bands at 1725.22 cm^{-1} and 1625.02 cm^{-1} were associated to the presence of carbonyl group ($\text{C}=\text{O}$) and hydroxyl (O-H) group stretching, respectively (Rathore et al. 2014). A new distinct $-\text{CH}_3$ bond was found at 1330 cm^{-1} (Mubashir et al. 2018). The heightened increase in peak intensity of the following functional groups in MMM-0.1F in comparison to blend CA-polymer and MMM-0.1P is attributed to the presence of the $-\text{OH}$ group from the functionalization agent, beta cyclodextrin ($\beta\text{-CD}$) and the presence of aromatic carbon-rings in the functionalized MWCNTs (Del Valle 2004).

Figure 2: ATR-FTIR of blend CA polymer (Blend CA-M), pristine MMM (MMM-0.1P) and functionalized MMM (MMM-0.1F) at casting thickness of 250 μm .

3.1.3 Membrane Gas Separation Performance for CO_2/N_2

As observed in Figure 3, gas separation performances for CO_2 were tested for blend CA-M, MMM-0.1P and MMM-0.1F. Based on Figure 3, blend CA-M demonstrated a good permeance rate towards CO_2 . When MWCNTs-P was integrated into the CA polymer, the separation performance of the CO_2 permeance significantly decreased from $144.812 \pm 3.03 \text{ GPU}$ to $133.601 \pm 2.23 \text{ GPU}$ in relative to the blend CA-M, respectively. This could be due to the alteration towards in distorted pattern associated with the polymer matrix that occurred, resulting from the embedding of impermeable MWCNTs-P (Ahmad et al. 2014; Lee et al. 2018). With the embedding of MWCNTs-F into the polymer matrix, gas permeance towards CO_2 dramatically increased to $415.995 \pm 5.14 \text{ GPU}$. The increment of the CO_2 permeance was influenced by the disturbance of the polymer chain packing as this has led to additional developments of free volume cavities between the polymer chains and between the polymer/nanofiller interface as well (Alexandre and Dubois 2000). As seen from Figure 2, the enhancement in polar functional groups such as carbonyl ($\text{C}=\text{O}$) group and hydroxyl (O-H) group greatly increased the dipole interactions by physisorptive manner by enhancing the sorption capacity of CO_2 (Shan et al. 2012). Hence, the CO_2 permeance for MMM-0.1F improved.

Meanwhile, the separation performance of N_2 permeance is presented for blend-CA, MMM-0.1P and MMM-0.1F membrane in Figure 3. It could be seen that the N_2 permeance for MMM-0.1F was significantly

Figure 3: Gas separation properties of polymeric membrane (Blend-CA), pristine MMM (0.1P) and functionalized MMM (0.1F) based on CO_2 permeance, N_2 permeance and CO_2/N_2 selectivity. Permeance tests were conducted at a constant thickness of 250 μm with constant feed gas supply.

lower compared to blend-CA membrane and MMM-0.1P. The low affinity towards N_2 gas was possibly due to result of the non-covalent functionalization of MWCNTs that favoured less N_2 (Lee et al. 2018). On the other hand, the MMM-0.1P demonstrated a higher permeance of N_2 in comparison to MMM-0.1F and blend-CA membrane. In a previous published work, Ahmad et al. (2014) stated that the high affinity towards N_2 gas may be attributed by the aggregated pores due to the integration of MWCNTs-P into the CA polymer matrix resulting in high adsorption capabilities.

The performance of CO_2/N_2 gas separation for blend-CA, MMM-0.1P and MMM-0.1F is observed in Figure 3. As indicated in this Figure, blend-CA, MMM-0.1P and MMM-0.1F were able to achieve ideal selectivity of 1.054 ± 0.026 , 0.951 ± 0.026 and 3.084 ± 0.019 , respectively. MMM-0.1F was able to achieve a greater separation performance as compared to MMM-0.1P and blend CA-M. Sarraz and Ba-Shammakh (2018) stated that the enhancement of the overall diffusivity of CO_2 gas was attributed to the close packing from the inherently smooth cylindrical walls of the CNTs. Thus, the permeance of CO_2 ($415.995 \pm 5.14 \text{ GPU}$) was higher compared to the N_2 gas ($134.872 \pm 0.903 \text{ GPU}$) which, resulted in the improvement of CO_2/N_2 selectivity performances (Sarraz and Ba-Shammakh 2018). Furthermore, the strong compatibility of MWCNTs with the CA polymer matrix resulted in the highly favored adsorption of CO_2 gas molecules as compared to N_2 molecules. Apart from the synergistical relationship between the CNTs with the CA polymer matrix, the capsulation of CO_2 was further improved due to the presence of the polar functional -OH group that possessed high affinity towards such gases resulting from the functionalization of MWCNTs with βCD (Lee et al. 2018; Trotta et al. 2011; Ahmad et al. 2014). However, MMM-0.1P showed relatively low gas separation performance as compared to MMM-0.1F and blend CA-M which were affected by the aggregation of MWCNTs-P (Khan et al. 2018). As a result, the lower selectivity of CO_2/N_2 was mainly due to the high amounts of N_2 gas being adsorbed from the aggregated pores of the impermeable MWCNTs-P (Khan et al. 2012).

3.2 Effect of different concentration loadings of MWCNTs-F

3.2.1 Membrane Physical Morphologies

As the integration of MWCNTs-F into CA polymer matrix improved the separation properties such as permeance and selectivity, the present study was extended to investigate the effects of different concentration loadings of MWCNTs-F to the performance of blend MMMs. The blend MMMs were fabricated with various loadings of MWCNTs-F. Figure 4 (a, c, e and g) shows the surface morphologies of the blend MMMs with different concentration loadings of MWCNTs, which are 0.05 wt% (MMM-0.05F), 0.15 wt% (MMM-0.15), 0.20 wt% (MMM-0.2F) and 0.30 wt% (MMM-0.3F). When low concentration loadings of MWCNTs were embedded into the blend CA polymer (0.05 wt%, MMM-0.05F), a nearly smooth surface with absence of defects were observed on these kind of membranes. However, as higher loadings of MWCNTs-F of 0.3 wt% (MMM-0.3F) was integrated into the CA polymer, these membranes showed a defected surface with large clusters of MWCNTs-F. In this case, the strong interactions between the MWCNTs particles induced by the Van der Waals forces led to the agglomeration which in turn, caused large

Figure 4: SEM cross section and surface morphologies for different loadings of MWCNTs-F in mixed matrix membrane (a and b) 0.05 wt% (MMM-0.05F), (c and d) 0.15 wt% (MMM-0.15F), (e and f) 0.20 wt% (MMM-0.20F) and (g and h) 0.30 wt% (MMM-0.3F). The membranes were fabricated at a constant thickness of 250 μm.

clusters to appear on the membrane surface (Lee et al. 2018). Furthermore, the MWCNTs were not distributed evenly and this led to an increased chance of agglomeration (Weng et al. 2009).

The membrane thickness of MMM-0.05F (b), MMM-0.15F (d), MMM-0.20F (f) and MMM-0.30F (h) are shown in Figure 4. The thickness of these membranes are found to be $6.591 \pm 0.19 \mu\text{m}$, $6.11 \pm 0.024 \mu\text{m}$, $5.76 \pm 0.022 \mu\text{m}$ and $7.23 \pm 0.29 \mu\text{m}$, respectively. When low contents of MWCNTs-F were incorporated in the CA polymer (0.05 wt% to 0.20 wt%), the MMMs exhibited decreasing overall thickness from $6.59 \pm 0.019 \mu\text{m}$ to $5.76 \pm 0.022 \mu\text{m}$ in the dense skin layer. The homogenous dispersion of MWCNTs-F into the polymer matrix could be the contributing factor towards the decreasing thickness in dense skin layer, as discussed earlier in Figure 1. This might also be due to the superior interaction between the MWCNTs-F and the polymer interface (Sarraz and Ba-Shammakh 2018).

However, when loadings of MWCNTs-F (0.3 wt%, MMM-0.3F) were embedded into the CA matrix, the thickness of the dense skin layer dramatically increased to $7.23 \pm 0.029 \mu\text{m}$ in comparison to MMM-0.05F, MMM-0.15F and MMM-0.20F. This was attributed to the phenomenon of the aggregation of MWCNTs-F when loadings were increased to 0.3 wt% (Ahmad et al. 2014). In accordance to Sarraz and Ba-Shammakh (2018), the MWCNTs-F were distributed poorly and were force embedded into the polymer matrix. Hence, stronger interactions between the MWCNTs ($\Pi = \Pi$ interaction) due to the Van der Waals forces in relation to the polymer matrix led to the occurrence of high aggregation (Lee et al. 2018).

3.2.2 Membrane Characterization (ATR-FTIR)

The infrared spectrum of functionalized MMM at different concentration loadings of 0.05 wt% (MMM-0.05F), 0.15 wt% (MMM-0.15F), 0.20 wt % (MMM-0.2F) and 0.30 wt% (MMM-0.30F) at 250 μm thickness are compared in Figure 5.

Figure 5: ATR-FTIR of functionalized MMM with different concentration loadings of MWCNTs-F 0.05 wt% (MMM-0.05F), 0.15 wt% (MMM-0.15F), 0.20 wt % (MMM-0.2F) and 0.30 wt% (MMM-0.30F) at casting thickness of 250 μm .

3.2.3 Membrane Gas Separation Performance for CO_2/N_2

The MMM with different loadings of MWCNTs-F varying from 0.05 wt% to 0.30 wt% and tested with CO_2 gas are shown in Figure 6. At 0.05 wt%, 0.15 wt% and 0.2 wt% loadings of MWCNTs-F, the CO_2 permeance increased significantly from $417.671 \pm 2.81 \text{ GPU}$, $425.068 \pm 6.69 \text{ GPU}$ to $476.341 \pm 7.15 \text{ GPU}$, respectively. The increase in the CO_2 permeance was due to the reduction of the membrane thickness corresponding to the superior interaction from the integration of MWCNTs-F into the polymer matrix (Khan et al. 2012). Furthermore, a thinner membrane thickness is preferable for gas separation as it imposes less flow resistance towards the permeating gas (Lee et al. 2018; Jawad et al. 2015).

On the other hand, CO_2 permeance was reduced drastically to $211.428 \pm 3.03 \text{ GPU}$ when the loading was further increased to 0.3 wt%. The MMM with loadings of 0.3 wt% MWCNTs-F (MMM-0.3F) showed lower peak intensity in the ATR-FTIR analysis in Figure 5 in comparison to the other MMMs. Hence, this indicated lesser amounts of carboxyl ($\text{C}=\text{O}$) and hydroxyl groups ($\text{O}-\text{H}$) that might have caused overall permeance of CO_2 to decrease for MMM-0.3F as compared to the other membranes (Lee et al. 2018). Nonetheless, the reduction of CO_2 permeance might also be due to the partial blockage of the sieve pores and the reduction of polymer chains mobility (Ismail et al. 2011; Ahmad et al. 2014). According to Casado Coterrillo et al. (2018), this contributed

to the compact packing and significantly denser skin layer of MMM-0.3F resulting in greater flow resistance towards CO_2 .

Figure 6 demonstrates the N_2 permeance with different MWCNTs loadings. It is observed that the N_2 permeance reduced from 140.68 ± 1.688 to $127.97 \pm 1.36 \text{ GPU}$ when concentration loading of 0.05 wt% (MMM-0.05) was increased to 0.20 wt% (MMM-0.2F). The effective integration of MWCNTs-F into the CA polymer chains significantly decreased the overall N_2 permeance rate (Ahmad et al. 2014). As observed in Figure 5, the peak enhancement of the functional groups such as the hydroxyl group ($\text{O}-\text{H}$) and carboxyl group ($\text{C}=\text{O}$) from loadings of 0.05 wt% to 0.20 wt% had less affinities towards gases such as N_2 due to the same polar bondings (Lee et al. 2018). Furthermore, the highest peak intensity was observed at 0.2 wt% loading (MMM-0.2F) resulting in the lowest N_2 permeance due to the significantly greater amounts of polar functional groups (Idris et al. 2017).

Figure 6: Gas separation properties of mixed matrix membrane fabricated with different MWCNTs-F loadings of 0.05 wt% (MMM-0.1F), 0.15 wt% (MMM-0.15F), 0.20 wt% (MMM-0.20F) and 0.30 wt % (MMM-0.3F) based on CO_2 permeance, N_2 permeance and CO_2/N_2 selectivity. Permeance tests were conducted at a constant thickness of 250 μm with constant feed gas supply.

In contrast, the N_2 permeance notably increased when 0.3 wt% MWCNTs-F are loaded into the CA polymer. This might be due to the excessive aggregation induced by the strong attractive forces between the MWCNTs which caused an increase in the overall N_2 permeance (Latif Ahmad et al. 2013). Nevertheless, the relatively higher N_2 permeance was also due to the lower peak intensity towards polar functional groups resulting in lower repelling force towards the polar gases such as N_2 (Trotta et al. 2011).

The CO_2/N_2 selectivity with different loadings of MWCNTs-F is presented in Figure 6. With regards to MMM-0.05F, MMM-0.15F, and MMM-0.2F, the CO_2/N_2 selectivity increased significantly from 2.97 ± 0.03 , 3.18 ± 0.09 , and 3.72 ± 0.014 , respectively. The significant increment in the selectivity from MMM-0.05F to MMM-0.2F matches the phenomenon of a superior synergistically relationship between the MWCNTs, polymer chains and the functionalization agent, βCD (Trotta et al. 2011; Lee et al. 2018). Furthermore, the reduction of overall resistance towards the CO_2 gas might also be due to the decreasing thickness of the dense skin layer ($6.59 \pm 0.019 \mu\text{m}$ to $5.76 \pm 0.022 \mu\text{m}$) from MMM-0.05F to MMM-0.2F which is explained and shown in Figure 4. Thus, the permeance of CO_2 was much higher compared to N_2 resulting in increased CO_2/N_2 selectivity (Lee et al. 2018).

In the case of over-loaded fillers (MMM-0.3F) resulting in lower CO_2/N_2 selectivity, the strong interaction in the particles itself throughout the polymer fillers led to poor adhesion causing the MWCNTs fillers to be distributed heterogeneously throughout the CA polymer (Ahmad et al. 2014). Hence, the poor dispersion of fillers throughout the fillers had caused less gas molecules to diffuse due to less availability of filler surface area (Ahmad et al. 2014). Based on Lee et al. (2018), this allowed less CO_2 molecules to permeate through the membrane due to the accessible pathway being compromised.

3.3 Comparison of CO_2/N_2 gas separation performance with present work and other published works

The CO_2/N_2 gas separation performance of the present study was compared to Shin Tien Lee et al. (2019), as tabulated in Table 2. Shin

Table 2: Summary of gas separation properties from present work compared to previous study

References	Polymer	Loadings of filler	P (CO ₂)(GPU)	P (N ₂)(GPU)	α (CO ₂ /N ₂)	Conditions
Present work	Blend CA (acetyl content of 39 wt% and 56 wt%)	MWCNTs-F 0.20 wt%	476.34	127.97	3.72	Temperature: 27°C Pressure: 1.0 to 3.0 x 10 ⁵ Pa
(Shin Tien Lee et al. 2019)	CAB (acetyl content of 28 wt% to 31 wt%)	1.10 wt%	351.15	119.81	2.93	

Tien Lee et al. (2019) had synthesized a MMM by utilizing cellulose acetate butyrate (CAB) of acetyl content of 28wt% to 31 wt% with loadings of 0.1wt% MWCNTs-F. The present study showed an increment of separation performance of 35.7% and 26.9% based on CO₂ permeance and selectivity, respectively. The superior separation properties were attributed to the average higher acetyl content of 49.2 wt % as per calculation from equation (1) in comparison to an average of 29.5 wt% from Shin Tien Lee et al. (2019). Furthermore, the strong interaction between the polymer matrix and the inorganic fillers, MWCNTs-F also contributed to the enhanced separation properties that resulted in important implications in the latter (Ahmad et al. 2014). Additionally, based on Simplicito et al. (2014), this separation ability between CO₂ and N₂ under single gas and binary gas mixtures would be similar in terms of permeance and selectivity.

4. Conclusions

In conclusion, it has been proven that the separation performance of CO₂/N₂ had improved from the functionalization of MWCNTs with α -CD. The optimal selectivity from the functionalization of MWCNTs (MWCNTs-F) was 3.084 + 0.019 with CO₂ permeance and N₂ permeance of 415.995 + 5.14 (GPU) and 134.872 + 0.903 (GPU), respectively. Hence, the study was extended to illustrate the effects of MWCNTs-F loadings to optimize the gas separation performance. By increasing the filler loadings to 0.2 wt% (MMM-0.2F), it significantly demonstrated enhanced gas separation performance of CO₂ permeance of 476.34 + 7.15 (GPU) and -N₂ permeance rate of 127.97 + 1.36 (GPU). The optimal selectivity obtained was 3.72 + 0.014 which was mainly attributed to the relatively thin skin dense layer and the synergistical relationship between the MWCNTs-F and the CA polymer. In addition, the optimum membrane with the incorporation of 0.2 wt % MWCNTs loading was able to provide increased separation properties of CO₂/N₂ gases which leads to valuable insights towards the cement production industry.

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References

- Ahmad, A. L., Z. A. Jawad, S. C. Low, and S. H. S. Zein. 2014. "A Cellulose Acetate/Multi-Walled Carbon Nanotube Mixed Matrix Membrane for Co₂/N₂ Separation." *Journal of Membrane Science* 451: 55-66. doi: <https://doi.org/10.1016/j.memsci.2013.09.043>.
- Alexandre, Michael, and Philippe Dubois. 2000. "Polymer-Layered Silicate Nanocomposites: Preparation, Properties and Uses of a New Class of Materials." *Materials Science and Engineering: R: Reports* 28 (1): 1-63. doi: [https://doi.org/10.1016/S0927-796X\(00\)00012-7](https://doi.org/10.1016/S0927-796X(00)00012-7).
- Allinson, Ken, Dan Burt, Lisa Campbell, Lisa Constable, Mark Crombie, Arthur Lee, Vinicius Lima, Tim Lloyd, and Lee Solsbey. 2017. "Best Practice for Transitioning from Carbon Dioxide (Co₂) Enhanced Oil Recovery Eor to Co₂ Storage." *Energy Procedia* 114: 6950-6956. doi: <https://doi.org/10.1016/j.egypro.2017.03.1837>.
- Aroon, M. A., A. F. Ismail, T. Matsuura, and M. M. Montazer-Rahmati. 2010. "Performance Studies of Mixed Matrix Membranes for Gas Separation: A Review." *Separation and Purification Technology* 75 (3): 229-242. doi: <https://doi.org/10.1016/j.seppur.2010.08.023>.
- Barker, D. J., S. A. Turner, P. A. Napier-Moore, M. Clark, and J. E. Davison. 2009. "Co₂ Capture in the Cement Industry." *Energy Procedia* 1: 87-94. doi: <https://doi.org/10.1016/j.egypro.2009.01.014>.
- Belaissaoui, Bouchra, and Eric Favre. 2014. "Membrane Separation Processes for Post-Combustion Carbon Dioxide Capture: State of the Art and Critical Overview." *Oil and Gas Science and Technology* 69 (6): 1005-1020. <http://dx.doi.org/10.2516/ogst/2013163>.
- Caro, J., M. Noack, P. Kölsch, and R. Schäfer. 2000. "Zeolite Membranes – State of Their Development and Perspective." *Microporous and Mesoporous Materials* 38 (1): 3-24. doi: [https://doi.org/10.1016/S1387-1811\(99\)00295-4](https://doi.org/10.1016/S1387-1811(99)00295-4).
- Casado Coterillo, Clara, Ana Fernández-Barquín, Susana Valencia, and Angel Irabien. 2018. *Estimating Co₂/N₂ Permselectivity through Si/Al = 5 Small-Pore Zeolites/ Ptmpp Mixed Matrix Membranes: Influence of Temperature and Topology*. Vol. 82.
- Chung, Tai-Shung, Lan Ying Jiang, Yi Li, and Santi Kulprathipanja. 2007. "Mixed Matrix Membranes (Mmms) Comprising Organic Polymers with Dispersed Inorganic Fillers for Gas Separation." *Progress in Polymer Science* 32 (4): 483-507. doi: <https://doi.org/10.1016/j.progpolymsci.2007.01.008>.
- Del Valle, E. M. Martin. 2004. "Cyclodextrins and Their Uses: A Review." *Process Biochemistry* 39 (9): 1033-1046. doi: [https://doi.org/10.1016/S0032-9592\(03\)00258-9](https://doi.org/10.1016/S0032-9592(03)00258-9).
- Ferraz, André, Jaime Baeza, Jaime Rodríguez, and Juanita Freer. 2000. *Estimating the Chemical Composition of Biodegradable Pine and Eucalyptus Wood by Drift Spectroscopy and Multivariate Analysis*. Vol. 74.
- George, Gigi, Nidhika Bhorla, Sama AlHallaq, Ahmed Abdala, and Vikas Mittal. 2016. "Polymer Membranes for Acid Gas Removal from Natural Gas." *Separation and Purification Technology* 158: 333-356. doi: <https://doi.org/10.1016/j.seppur.2015.12.033>.
- Idris, Alamin, Zakaria Man, Abdulhalim S. Maulud, and Muhammad Saad Khan. 2017. "Effects of Phase Separation Behavior on Morphology and Performance of Polycarbonate Membranes." *Membranes* 7 (2): 21. doi: <https://doi.org/10.3390/membranes7020021>.
- Ismail, A. F., N. H. Rahim, A. Mustafa, T. Matsuura, B. C. Ng, S. Abdullah, and S. A. Hashemifard. 2011. "Gas Separation Performance of Polyethersulfone/Multi-Walled Carbon Nanotubes Mixed Matrix Membranes." *Separation and Purification Technology* 80 (1): 20-31. doi: <https://doi.org/10.1016/j.seppur.2011.03.031>.
- Ismail, Ahmad, and Lai Ping Yean. 2003. *Review on the Development of Defect Free and Ultrathin Skinned Asymmetric Membranes for Gas Separation through Manipulation of Phase Inversion and Rheological Factors*. Vol. 88.
- Jawad, Z. A., Abdul Latif Ahmad, Siew Chun Low, and Sharif Zein. 2015. *Incorporation of Inorganic Carbon Nanotubes Fillers into the Ca Polymeric Matrix for Improvement in Co₂/N₂ Separation*. Vol. 11.
- Kamal, H., F. M. Abd-Elrahman, and S. Lotfy. 2014. "Characterization and Some Properties of Cellulose Acetate-Co-Polyethylene Oxide Blends Prepared by the Use of Gamma Irradiation." *Journal of Radiation Research and Applied Sciences* 7 (2): 146-153. doi: <https://doi.org/10.1016/j.jrras.2014.01.003>.
- Khan, Muntazim Munir, Volkan Filiz, Gisela Bengtson, Sergey Shishatskiy, Mushfequr Rahman, and Volker Abetz. 2012. "Functionalized Carbon Nanotubes Mixed Matrix Membranes of Polymers of Intrinsic Microporosity for Gas Separation." *Nanoscale Research Letters* 7 (1): 504. doi: <https://doi.org/10.1186/1556-276X-7-504>.
- Khan, Muntazim Munir, Sergey Shishatskiy, and Volkan Filiz. 2018. "Mixed Matrix Membranes of Boron Icosahedron and Polymers of Intrinsic Microporosity (Pim-1) for Gas Separation." *Membranes* 8 (1): 1. doi: <https://doi.org/10.3390/membranes8010001>.
- Kim, Seungju, Jue Hou, Yuqi Wang, Ranwen Ou, George P. Simon, Jong Geun Seong, Young Moo Lee, and Huanting Wang. 2018. "Highly Permeable Thermally Rearranged Polymer Composite Membranes with a Graphene Oxide Scaffold for Gas Separation." *Journal of Materials Chemistry A* 6 (17): 7668-7674. doi: <https://doi.org/10.1039/C8TA02256A>.
- Latif Ahmad, Abdul, Zeinab Abbas Jawad, Siew Chun Low, and Sharif Hussein Sharif Zein. 2013. "The Functionalization of Beta-Cyclodextrins on Multi Walled Carbon Nanotubes: Effects of the Dispersant and Non Aqueous Media." *Current Nanoscience* 9 (1): 93-102. doi: <https://doi.org/10.2174/157341313805117839>.
- Lee, R. J., Z. A. Jawad, A. L. Ahmad, and H. B. Chua. 2018. "Incorporation of Functionalized Multi-Walled Carbon Nanotubes (Mwcnts) into Cellulose Acetate Butyrate (Cab) Polymeric Matrix to Improve the Co₂/N₂ Separation." *Process Safety and Environmental Protection* 117: 159-167. doi: <https://doi.org/10.1016/j.psep.2018.04.021>.

- [23] Mardani, Abbas, Dalia Streimikiene, Fausto Cavallaro, Nanthakumar Loganathan, and Masoumeh Khoshnoudi. 2019. "Carbon Dioxide (Co₂) Emissions and Economic Growth: A Systematic Review of Two Decades of Research from 1995 to 2017." *Science of The Total Environment* 649: 31-49. doi: <https://doi.org/10.1016/j.scitotenv.2018.08.229>.
- [24] Mubashir, Muhammad, Yin Fong Yeong, C. T. Leng, and Kok Keong Lau. 2018. *Enhanced Gases Separation of Cellulose Acetate Membrane Using N-Methyl-1-2 Pyrrolidone as Fabrication Solvent*. Vol. 15.
- [25] Omid, Meisam, Atena Fatehiny, Masomeh Farahani, Zahra Akbari, Saleheh Shahmoradi, Fatemeh Yazdian, Mohammadreza Tahriri, Keyvan Moharamzadeh, Lobat Tayebi, and Daryoosh Vashae. 2017. "7 - Characterization of Biomaterials." In *Biomaterials for Oral and Dental Tissue Engineering*, eds Lobat Tayebi and Keyvan Moharamzadeh, 97-115. Woodhead Publishing.
- [26] Pieslesz, A., and W. Biniac. 2010. "Cellulose Acetate Membrane Electrophoresis and Ftir Spectroscopy as Methods of Identifying a Fucoidan in Fucus Vesiculosus Linnaeus." *Carbohydrate Research* 345 (18): 2676-2682. doi: <https://doi.org/10.1016/j.carres.2010.09.027>.
- [27] Powell, Clem E., and Greg G. Qiao. 2006. "Polymeric Co₂/N₂ Gas Separation Membranes for the Capture of Carbon Dioxide from Power Plant Flue Gases." *Journal of Membrane Science* 279 (1): 1-49. doi: <https://doi.org/10.1016/j.memsci.2005.12.062>.
- [28] Rathore, Bhim Singh, Gaurav Sharma, Deepak Pathania, and Vinod Kumar Gupta. 2014. "Synthesis, Characterization and Antibacterial Activity of Cellulose Acetate-Tin (Iv) Phosphate Nanocomposite." *Carbohydrate Polymers* 103: 221-227. doi: <https://doi.org/10.1016/j.carbpol.2013.12.011>.
- [29] Sahoo, Nanda Gopal, Sravendra Rana, Jae Whan Cho, Lin Li, and Siew Hwa Chan. 2010. "Polymer Nanocomposites Based on Functionalized Carbon Nanotubes." *Progress in Polymer Science* 35 (7): 837-867. doi: <https://doi.org/10.1016/j.progpolymsci.2010.03.002>.
- [30] Sangeetha, A., and T. Amudha. 2018. "A Novel Bio-Inspired Framework for Co₂ Emission Forecast in India." *Procedia Computer Science* 125: 367-375. doi: <https://doi.org/10.1016/j.procs.2017.12.048>.
- [31] Sanglimsuwan, K. 2011. "Carbon Dioxide Emissions and Economic Growth: An Econometric Analysis." *International Research Journal of Finance and Economics* 67: 97-102. <https://www.scopus.com/inward/record.uri?eid=2-s2.0-79958038257&partnerID=40&md5=4ecb12f7333d009c96422ed04787cb9e>.
- [32] Sarfraz, Muhammad, and Mohammed Ba-Shammakh. 2018. "Harmonious Interaction of Incorporating Cnts and Zeolitic Imidazole Frameworks into Polysulfone to Prepare High Performance Mmms for Co₂ Separation from Humidified Post Combustion Gases." *Brazilian Journal of Chemical Engineering* 35: 217-228. http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322018000100217&nrm=iso.
- [33] Shan, Meixia, Qingzhong Xue, Nuannuan Jing, Cuicui Ling, Teng Zhang, Zifeng Yan, and Jingtang Zheng. 2012. "Influence of Chemical Functionalization on the Co₂/N₂ Separation Performance of Porous Graphene Membranes." *Nanoscale* 4 (17): 5477-5482. doi: 10.1039/C2NR31402A.
- [34] Shin Tien Lee, Jia Ni Pang, and Zeinab Abbas Jawad. 2019. "Functionalised Multi-Walled Carbon Nanotubes/Cellulose Acetate Butyrate Mixed Matrix Membrane for Co₂/N₂ Separation." *Journal of Physical Science*, 30(2)..
- [35] Silva, Elisângela Aparecida da, Dario Windmöller, Glauro Goulart Silva, and Kátia Cecília de Souza Figueiredo. 2017. "Polydimethylsiloxane Membranes Containing Multi-Walled Carbon Nanotubes for Gas Separation." *Materials Research* 20: 1454-1460. http://www.scielo.br/scielo.php?script=sci_arttext&pid=S1516-14392017000601454&nrm=iso.
- [36] Simplicio, Manuel, Maria Diná Afonso, Olga Borisevich, Xavier Lefebvre, and David Demange. 2014. "Permeation of Single Gases and Binary Mixtures of Hydrogen and Helium through a Mfi Zeolite Hollow Fibres Membrane for Application in Nuclear Fusion." *Separation and Purification Technology* 122: 199-205. doi: <https://doi.org/10.1016/j.seppur.2013.10.034>.
- [37] Songolzadeh, Mohammad, Mansoor Soleimani, Maryam Takht Ravanchi, and Reza Songolzadeh. 2014. "Carbon Dioxide Separation from Flue Gases: A Technological Review Emphasizing Reduction in Greenhouse Gas Emissions." *The Scientific World Journal* 2014: 34. doi: 10.1155/2014/828131.
- [38] Trotta, Francesco, Roberta Cavalli, Katia Martina, Miriam Biasizzo, Jenny Vitillo, Silvia Bordiga, Pradeep Vavia, and Khalid Ansari. 2011. "Cyclodextrin Nanosponges as Effective Gas Carriers." *Journal of Inclusion Phenomena and Macrocyclic Chemistry* 71 (1): 189-194. doi: 10.1007/s10847-011-9926-5.
- [39] Wang, Meng-Jiao. 1998. "Effect of Polymer-Filler and Filler-Filler Interactions on Dynamic Properties of Filled Vulcanizates." *Rubber Chemistry and Technology* 71 (3): 520-589. doi: 10.5254/1.3538492.
- [40] Weng, Tzu-Hsiang, Hui-Hsin Tseng, and Ming-Yen Wey. 2009. "Preparation and Characterization of Multi-Walled Carbon Nanotube/Pbnpi Nanocomposite Membrane for H₂/Ch₄ Separation." *International Journal of Hydrogen Energy* 34 (20): 8707-8715. doi: <https://doi.org/10.1016/j.ijhydene.2009.08.027>.