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Incorporation of functionalized multi-walled carbon nanotubes (MWCNTs) into cellulose acetate butyrate (CAB) polymeric matrix to improve the CO_2/N_2 separation

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ABSTRACT

Membrane-based technology has received much attention in the past decades due to attractive features offered. Through significant breakthroughs of this technology, the mixed matrix membrane (MMM) has demonstrated a promising carbon dioxide (CO_2)/nitrogen (N_2) separation performance. Among the polymer materials used, cellulose acetate butyrate (CAB) polymer was selected due to its outstanding characteristics, which subsequently could improve the CO_2 sorption ability. In this study, MMM was prepared by incorporating the functionalised multi-walled carbon nanotubes (MWCNTs-F) as inorganic material into the CAB polymer matrix (MMM-4F). The CAB membrane (CAB-M) was also synthesised under similar fabrication parameters via the phase-inversion method to determine the CO_2/N_2 separation performance. The gas permeation results showed that the CO_2/N_2 separation performance increased dramatically from 6.12 ± 0.09 to 11.00 ± 1.92 when 4 wt% of MWCNTs-F was incorporated into the CAB polymer matrix. The increase in CO_2 permeance within the MMM was due to the embedded MWCNTs-F within the CAB polymer matrix. In this study, the new synthesised MMM proved to possess excellent CO_2/N_2 separation performance. However, it could further be improved by manipulating the amount of MWCNTs-F incorporated into the CAB polymer matrix. This is suitable for the gas separation field.

1. Introduction

The rapid increase in the world population and growth in energy consumption throughout the 21st century, has led to the increase of greenhouse gases (GHGs) levels in the atmosphere. From the statistics shown in the past 15 years, the increase in GHGs levels in the atmosphere is believed to be the main source of global warming (Yang et al., 2008). Among these GHGs, carbon dioxide (CO_2) is considered particularly as the largest contributor towards the global warming effects (Yildirim and Hughes, 2003; Yamasaki, 2003). The emergence of global warming effects eventually raised global concerns. Much effort has been undertaken in the past few decades to mitigate this global warming issue to prevent undesirable impacts on Earth. Among all the technologies available to reduce the CO_2 emission into the atmosphere, the membrane-based technology appears to be one of the best technologies so far to capture and sequester more CO_2 since their first commercialised application in 1981, which targeted major industries. Notably, the type of polymer material that has been commercialised so far includes, polycarbonates, polysulfone, polyaramide, polyimide, cellulose acetate (CA), and others (Baker, 2002). With regards to the polymer materials mentioned, cellulose acetate butyrate (CAB) recently emerged as the new polymer material due to few outstanding characteristics exhibited (Cheng et al., 2006).

The highlighted features that CAB polymer possess includes high chemical and weather resistance, great film forming properties, and most importantly composition of butyryl and acetyl functional groups that can effectively improve and expand the capacity of the cellulose chain. Hence, high sorption characteristic (Kunthadong

Abbreviations: A, effective membrane area (m^2); α, ideal separation factor; ATR-FTIR, attenuated total reflectance Fourier-transform infrared spectroscopy; β-CD, beta-cyclodextrin; CA, cellulose acetate; CAB, cellulose acetate butyrate; CO_2, carbon dioxide; CMS, carbon molecular sieve; CNTs, carbon nanotubes; GHGs, greenhouse gases; GPU, gas permeation unit; l, membrane thickness (μm); mL, milliliter; MMM, mixed matrix membrane; MMMs, mixed matrix membranes; MWCNTs, multi-walled carbon nanotubes; MWCNTs-F, functionalized-multi-walled carbon nanotubes; MWCNTs-P, pristine-multi-walled carbon nanotubes; N_2, nitrogen; ΔP, pressure difference (Pa); P_{CO2}, permeability of carbon dioxide (mol/m^2 s Pa); P_{N2}, permeability of nitrogen (mol/m^2 s Pa); Q, volumetric flow rate; SEM, scanning electron microscopy; μm, micrometer.

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et al., 2015). However, the typical problem faced by most of the polymeric membranes is the adverse effect of trade-off relationship between permeability and selectivity and swelling phenomenon, which can alter the membrane separation properties (Goh et al., 2011). Therefore, to address the problems encountered by polymeric membranes, the mixed matrix membrane (MMM) was then introduced (Aroon et al., 2010a; Kentish et al., 2008).

In the MMM approach, the membrane was fabricated by incorporating inorganic fillers into polymer matrix (Moore et al., 2004). In the field of MMMs fabrication, the inorganic fillers that have been used extensively are activated carbon, zeolites, carbon molecular sieves (CMS), and carbon nanotubes (CNTs) (Abedini et al., 2018; Zhang et al., 2014; Goh et al., 2011). Among all the inorganic fillers, CNTs emerge as the most potential candidate for gas separation applications due to their superior mechanical properties and gas separation efficiency (Aroon et al., 2013).

Since the beginning of the 1990s, CNTs have been exploited and applied in different fields (Aroon et al., 2010a). However, the full potential of CNTs has been hindered because of their chemically inert properties, and their ability to disperse in the common organic solvents. Hence, creating a major drawback for CNTs (Ahmad et al., 2014). Consequently, much effort has been focused on functionalisation work of CNTs to advance their dispersion within the polymer matrix (Sanip et al., 2011). Lately, it was found that the non-covalent functionalisation method was able to significantly increase the CNTs dispersion within the polymer matrix utilising Chen's Soft Cutting method (Chen et al., 2001). Moreover, using the beta-cyclodextrins (β-CD) to improve the functionality of multi-walled CNTs (MWCNTs) has shown promising gas separation results as reported in several published works (Ismail et al., 2009; Jawad et al., 2015a; Goh et al., 2011).

The aim of the present work is to synthesise a new MMM by incorporating the functionalised MWCNTs (MWCNTs-F) into the CAB polymer matrix. Through this study, this novel MMM (CAB/MWCNTs-F) is expected to demonstrate high separation performance towards CO_2/N_2 separation. Up to date, no reports have mentioned the separation performance by incorporating MWCNTs into CAB polymer matrix. This MMM is expected to exhibit high permeance and selectivity performance, thereby inheriting the high CO_2 sorption ability from CAB polymer matrix and superior mechanical properties from CNTs. In this study, the effect of incorporating MWCNTs-F into CAB polymer matrix was evaluated with neat CAB membrane. The separation properties of MMM (CAB/MWCNTs-F) and neat membrane (CAB-M) were then subsequently compared by calculating the CO_2/N_2 permeance and selectivity yield.

2. Methodology

2.1. Materials

Cellulose acetate butyrate (CAB) (acetyl content: 12–15 wt%) was purchased from Sigma-Aldrich (Malaysia) for membrane fabrication. Solvent chloroform (≥99.7%) was supplied by Merck (Malaysia). Beta-cyclodextrin (β-CD), isopropyl alcohol and *n*-hexane were acquired from Merck (Malaysia). Multi-walled carbon nanotubes (MWCNTs) (95%) with average outer and inner diameter of 26.62 nm and 8.85 nm respectively, were purchased from Shenzhen Nanotech Port Co. Ltd, China.

2.2. MWCNTs functionalisation (MWCNTs-F)

The functionalisation of MWCNTs was carried out by first drying them in an oven overnight at 120 °C to remove moisture. The dried MWCNTs were then functionalised using Chen's Soft Cutting method (Chen et al., 2001). Based on this functionalisation technique, pristine MWCNTs (MWCNTs-P) were grounded with mortar and pestle at a concentration ratio of 1:30 wt% β-CD. In the first 10 min of grinding, ethanol was gradually added to form a greyish sticky mixture. Further grinding was continued for another 2.5 h, resulting in a fine grey powder form, which was then heated in the oven at a temperature of 80 °C for 24 h to obtain the MWCNTs-F (Ahmad et al., 2014).

2.3. Fabrication of CAB membrane (CAB-M)

The neat membrane (CAB-M) was prepared by the wet-phase inversion method, followed by solvent exchange to dry the membrane. The dope solution was prepared with CAB powder and chloroform following the condition of each parameter. The solution was stirred for 24 h, and then sonicated for 20 min to eliminate the bubbles in the solution to ensure membrane morphology evenness (Feng et al. 2015). The membrane was then cast on glass plate using automatic film applicator. A 5 min solvent evaporation time was allowed before immersing the membrane into distilled water (27 °C) for 24 h (Lee et al., 2017). Subsequently, solvent exchange was performed on the as-spun membrane by immersing it in isopropyl alcohol for 60 min followed by immersion in *n*-hexane for another 60 min. The resultant membrane was thereafter dried at ambient temperature for 24 h before permeation test to eliminate the volatile liquid remaining in between two glass plates filled with filter paper (Ahmad et al., 2014).

2.4. Fabrication of mixed matrix membrane (MMM)

The MMM was prepared by adopting the wet-phase inversion method, and subsequently solvent exchange with solvents, to eliminate the moisture on the membrane. A specific amount of the solid base MWCNTs-F was added to the solvent chloroform and sonicated for 20 min. The mixture was then stirred for another 4 h with magnetic stirrer to ensure well-dispersed particle distribution (Aroon et al., 2010c). The CAB polymer was subsequently added into the mixture of MWCNTs-F with chloroform, and stirred for 24 h until the CAB polymer was completely dissolved in the mixture. The casting procedure was similar to the previous method mentioned in Section 2.3 (Lee et al., 2017). The composition for the membrane prepared is illustrated in Table 1.

2.5. Membrane permeation test

Pure carbon dioxide (CO_2) and nitrogen (N_2) gases were used for the single gas permeation test at ambient temperature. A schematic diagram of the experimental rig is shown in Fig. 1. The feed rate of each gas supplied from a compressed gas cylinder tank was controlled at 100 ml/minute using the mass flow controller (Aalborg AFC26, USA). The mass flow controller was connected to a two-channel digital set point readout unit (Aalborg 0–200 ml, USA) to display and further control the output flow of the feed gas. The feed gas pressure was set from 1 to 3 bars throughout the experimental investigation. Before starting the permeability test, gas leak detection test was conducted, to ensure that no feed gas escaped from the rig connecting pipes. Pure N_2 gas was used to flush and purge out any gases that remained in the gas pipes for duration of 15 min. After that, the prepared membrane was cut into a round disc shape with an effective diameter of 7.0 cm^2, and placed in the membrane permeation cell. The locks of the membrane permeation cell were tightened with alley keys before connecting them back to the feed streams. The gas permeance volume displacement was obtained and measured through the soap bubble flow meter with the use of a stopwatch to calculate the displacement time.