

Development of Polysulfone/Activated Carbon Nanofibers Mixed Matrix Membrane for CO₂/CH₄ Separation

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ABSTRACT

This study was performed primarily to investigate the effect of activated carbon nanofiber (ACNF) on carbon dioxide and methane separation performance of mixed matrix membrane (MMM). In this study, polysulfone (PSf)/ACNF mixed matrix membranes was fabricated using dry/wet inversion technique. The effect of PSf concentration and ACNF loading on the performance of mixed matrix membrane in terms of permeability and selectivity of CO₂/CH₄ gas separation was observed. The fabricated flat sheet mixed matrix membranes were characterized using Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) analysis. From the SEM observations, it shows that sponge like structures images were observed upon the addition of ACNFs in the PSf/ACNF membranes was slowly decreased due to increasing weight percentage of ACNF. FT-IR result indicating the presence of carboxyl group in MMM at wavelength 1750 cm⁻¹. Meanwhile, the MMMs were further tested to pure permeation test using pure CO₂ and CH₄ gas, the CO₂ permeance improved and the selectivity of CO₂/CH₄ increased after the addition of ACNFs.

Keywords: Activated carbon nanofiber, mixed matrix membrane, gas separation

1.0 INTRODUCTION

It is attractive to evacuate non-fuel gasses with a specific end goal to minimize operation costs and expand the heating value of the gas. Acid gasses, for example, carbon dioxide and hydrogen sulfide, must be expelled to avert consumption in pipelines and handling equipment. Carbon dioxide is the most bottomless contaminant in numerous gas stores, and by far most of regular gas separation look into has been committed to its evacuation [1]. As characteristic of natural gas request increments over the coming years, more effective separation innovations that permit expanded throughput with negligible handling expense was important to keep normal gas costs

manageable.

These days, there are a few set up procedures that have been presently connected to address this issue, for example, amine based absorption, potassium carbonate based absorption, cryogenic separation process, and membranes separation technology. [2] Each of the procedures offers diverse division components with specific favorable circumstances and limitations. The most broadly utilized procedure to sanitize natural gas uses alkanolamine aqueous solution to absorb specifically carbon dioxide and hydrogen sulphite from natural gas. This procedure is to great degree energy intensive and requires different steps arrangement for the separation and solution recovery including

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heating of the recovery acid gas [3]

Polymeric membranes are the most widely recognized membranes for gas separation process. There are already membrane systems installed for natural gas sweetening many places in the world, including offshore Malaysia [4]. However, the performances of polymeric membrane are limited to low productivity and trade off effects between selectivity/permeability. To address this issue, the development of mixed matrix membrane (MMM) membranes is proposed to overcome the limitation of polymeric membranes [5]. Combination of the organic (polymer) with inorganic materials give birth to a nanocomposite membranes which will possess the synergistic advantages from each phase: high selectivity and permeability of the dispersed fillers and easy processability of the polymers [6].

Herein, in this study we proposed ACNF to be incorporated in PSf membrane to study the effect of its physicochemical properties and their gas separation performances.

2.0 METHODS

2.1 Materials

Commercially available Polysulfone pellets (PSf; Udel P3500) were purchased from Solvay polymers as the membrane substrates polymer and 1,2-methyl pyrrolidone (NMP) and tetrahydrofuran (THF) were purchased from Merck as the solvent to dissolve the polymers. ACNF were produced by pyrolysis of NFs from polyacrylonitrile. The NFs were later carbonized at 600°C under nitrogen flow at heating rate of 5°Cmin⁻¹ to produce carbon nanofibers (CNFs). The CNFs were physically activated in horizontal tube furnace (Carbolite

CTF12/65/550) at temperature of 800°C under carbon dioxide flow at heating rate of 5°C min⁻¹ to yield activated carbon nanofibers (ACNFs) [6].

2.2 Preparation of Mixed Matrix Membrane

The fabrication of neat PSf and MMMs were adapted from Nordin *et al.* [7]. PSf pellets (25 wt%) was dissolved in NMP (37.5 wt%) and THF (37.5 wt%) solution at the room temperature for at least 12 h until the solution become homogeneous. For preparation of PSf/ACNFs MMMs, the loading of ACNFs was varied in a range from 0.0 wt% to 1.5 wt% per total weight of polymer. Table 1 referred to the summarized concentration used in this study. The ACNF powder were added in NMP (37.5 wt%) and THF (37.5 wt%) solution and stirred for 5 hours until the solution become homogenous. The PSf pellets were subsequently added in the mixture solution and stirred on the hot plate for at least 12 hours until the dope solution became homogenous. The dope solution was degassed at the room temperature to remove all air bubbles.

Table 1 Summarized concentrations for dope solution

Sample	PSf (wt%)	NMP (wt%)	THF (wt%)	ACNF (wt%)
1	25	37.5	37.5	0.0
2	25	37.5	37.5	0.1
3	25	37.5	37.5	0.5
4	25	37.5	37.5	1.0
5	25	37.5	37.5	1.5

A flat sheet membrane was prepared via dry/wet inversion technique using manual casting method. The dope solution was casted

on clean glass plate to form thin film 0.1 cm. After standing on the glass plate for approximately 3 min, the casted layer and the glass plate was immersed in a coagulation bath (deionized water) at room temperature where the membrane was solidified. After that the membranes was stored in fresh water bath for at least 1 day to leach out the residual solvents completely. Last step, the membrane was dried for 24 hours in the ambient atmosphere. The other membrane was prepared by the same process for sample 2, 3, 4 and 5 respectively as shown in the Figure 1.

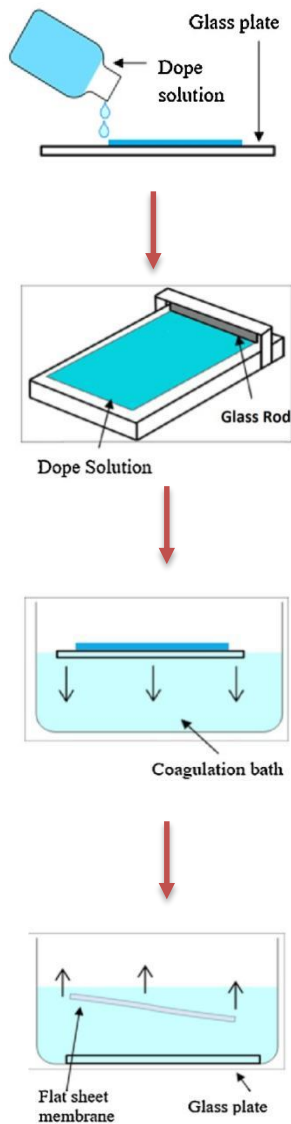


Figure 1 Steps in fabrication of flat sheet membrane

2.4 Characterization of MMMs

The neat membrane and MMMs was further characterized to understand their physicochemical properties. The membranes morphological structures were characterized by Scanning Electron Microscopy (SEM) with magnification 3.0k and 5.0k analysis with an accelerating voltage of 20.0 kV. Chemical functional group of neat and MMMs were analysed by using FTIR (Fourier Transform Infrared Spectroscopy) at wavelength about 400 cm⁻¹ to 4000 cm⁻¹ and 0.25 cm⁻¹ scanning resolution has been set.

2.5 Gas Permeation Test

Gas permeation system was made up to measure pure gas permeation rate for asymmetric flat sheet membrane and approximately their selectivity. Figure 2 illustrated the overall gas permeation system used in this study. Gas permeation test was prepared using two high purity (99.99%) of gas which is CO₂ and CH₄. The main objective is to determine the level of permeability of membrane based on volume displacement method at room temperature and low operating pressure. The permeation coefficient was determined by apply the following equation:

$$P_i = Q_i \times L / A \times \Delta P \quad (1)$$

where P_i is the permeability of gas permeation through the membrane which is expressed in GPU (1 GPU = 10⁻⁶ cm³STP/cm² s cm Hg); Q_i is volumetric gas flowrate of gas CO₂ and CH₄ (cm³/s); ΔP is pressure difference across membrane (cm Hg); L is thickness of membrane (cm) and A is effective membrane for permeation test (cm²).

Selectivity of prepared membrane was determined using following equation.

$$\alpha = P_i / P_j \quad (2)$$

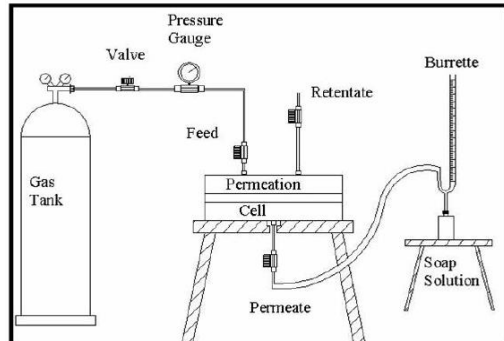


Figure 2 Gas permeation system

3.0 RESULTS AND DISCUSSION

3.1 Functional Group Analysis

The prepared neat PSF and ACNF MMMs were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) to identify chemical functional groups of fabricated membranes. Figure 3 illustrates the stretching band of MMMs which made by using various 0.0wt%, 0.1wt%, 0.5wt%, 1.0wt% and 1.5wt% of ACNF respectively. There are bands at around $1107\text{-}1092\text{ cm}^{-1}$ that indicated for the aromatic ring vibrations. The strong absorptions due to the asymmetric stretches of sulfone group in PSF molecule were found at round that range belong to the aromatic $\text{O}=\text{S}=\text{O}$ in polysulfone molecules. C-H stretching band sample that were detected at frequency around $3200\text{-}2800\text{ cm}^{-1}$ [8-9]. Membrane fabricated from mixture of PSf/NMP/ACNF showed positive attending of carboxylic group asymmetric $\text{C}=\text{O}$ that stretching of carboxylic acid group at frequency around $1780\text{ - }1710\text{ cm}^{-1}$. From the findings, it shows that the chemical functional that appears probably contributed to excellent permeability and selectivity.

3.2 Morphology and Structure of PSf/ACNF MMMs

The morphological structures of neat PSf and MMMs were analysed by using SEM analysis. As can be seen cross section images from Figure 4 (a-e), From the SEM images, all membranes exhibited partially sponge type porous structures. The porous structures of MMMs were slowly decreasing upon the addition of ACNFs as presented in Figure 4 (g-j). However, the presence of ACNFs are not detected by SEM images probably attributed to smaller size of ACNFs and well-distribution of this fillers in membrane matrix [10]. Meanwhile, Figure 4 (f-j) displayed the surface micrographs of neat membrane and ACNFs composite membranes. From the SEM images, all membranes show that pinhole appeared on the surface and decreasing as the loading of ACNFs is increasing. The appearances of pinhole on these surfaces probably contributed by non-uniform distribution of ACNFs in the membranes structures. However, as the loading of ACNFs is increasing the pinhole on the surface is slowly diminished.

3.2 Gas Separation Performance

To observe the effect of ACNFs-MMMs were further investigated by the gas separation performances methane and carbon dioxide. Based on the Table 2 presented below, shows the selectivity and permeability of membrane has improved as the loading of ACNFs is increased. The CO_2 permeability and CO_2/CH_4 selectivity of neat PSf are 20.51 GPU and 1.32 respectively. The lower permeability value and selectivity probably attributed to the different materials and fabrication methods [7].

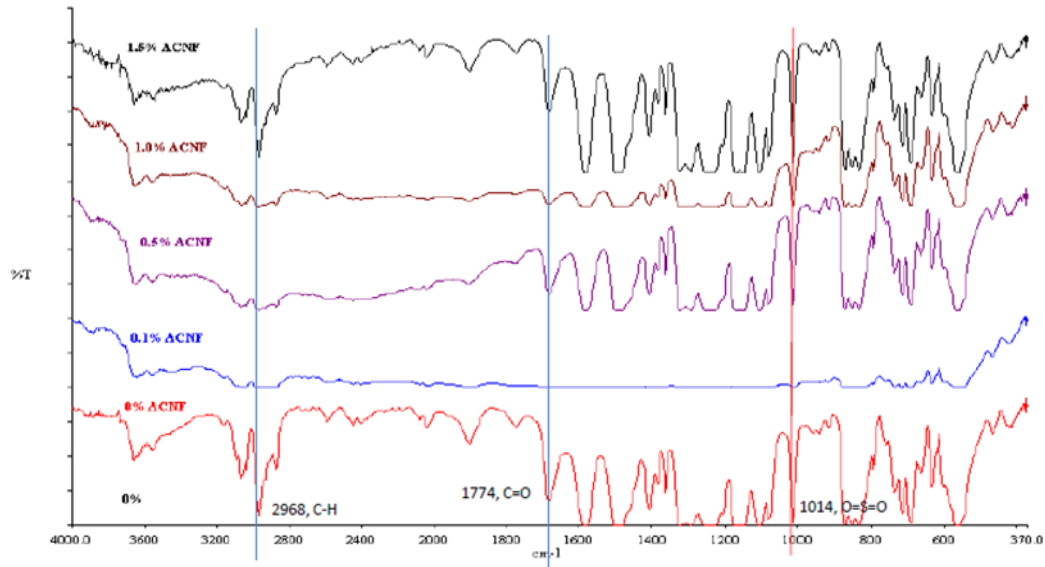


Figure 3 FTIR spectrums of neat membrane and MMMs membranes

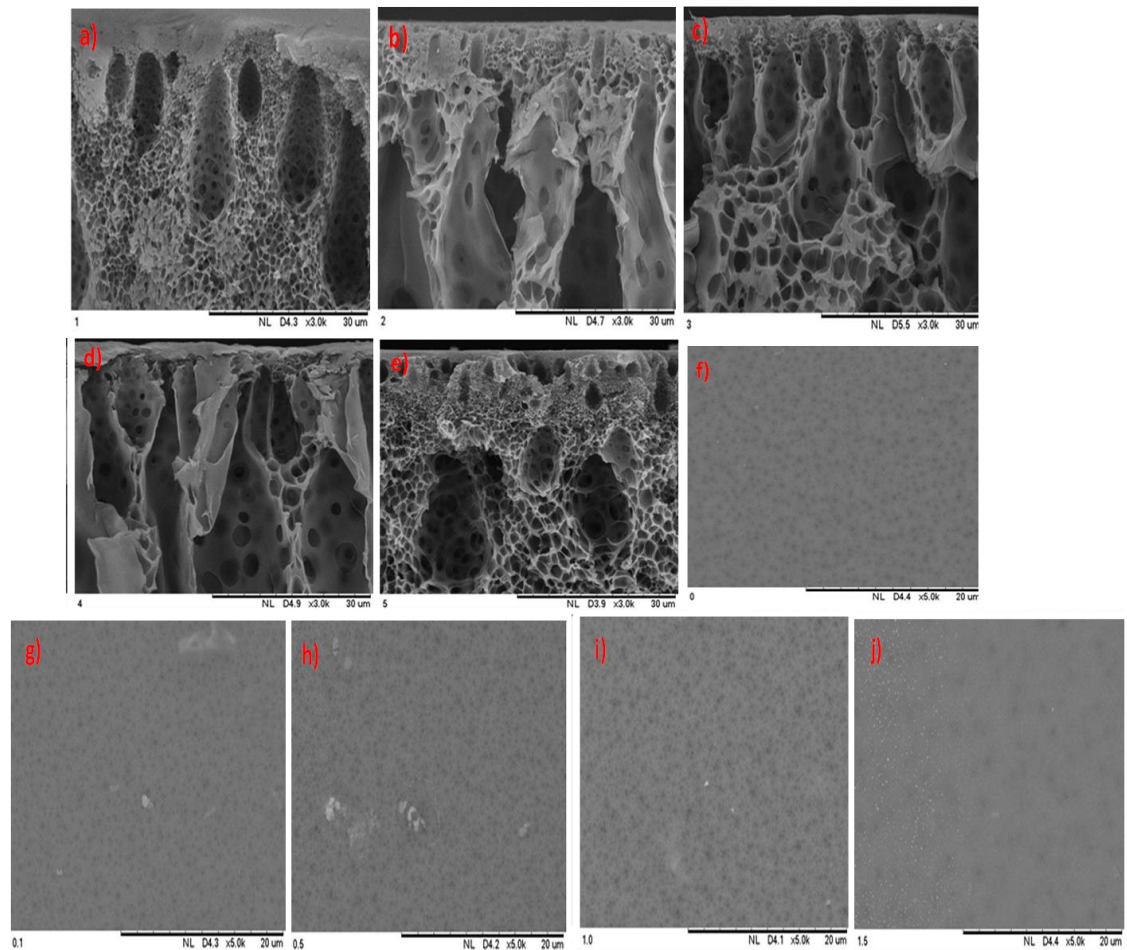


Figure 4 SEM images of cross-sections of polysulfone containing different concentration of ACNF (a) 0.0wt%, (b) 0.1wt%, (c) 0.5wt%, (d) 1.0wt%, (e) 1.5wt% and surface images of polysulfone containing different concentration of ACNF (f) 0.0wt%, (g) 0.1wt%, (h) 0.5wt%, (i) 1.0wt%, (j) 1.5wt%

Table 2 Permeability and selectivity of PSf and MMMs

Sample	Permeability (GPU)		Selectivity CO ₂ /CH ₄
	CO ₂	CH ₄	
Neat PSf	20.51	15.55	1.32
0.1 wt% ACNFs -MMM	22.45	16.39	1.37
0.5 wt% ACNFs -MMM	26.35	18.82	1.40
1.0 wt% ACNFs -MMM	30.81	21.00	1.41
1.5 wt% ACNFs -MMM	35.26	24.67	1.43

Upon the addition of ACNFs in polymer matrix, the CO₂ permeability and CO₂/CH₄ selectivity are slowly increased compared with neat PSf. [7]. The enhancement in permeability were assumed caused by the interaction between polymer and ACNFs that could distort the polymer chain packing thus resulting in increased of gas diffusion due to more free volumes introduced [10]. Furthermore, the CO₂/CH₄ selectivity increased after the addition of ACNFs. The increased in selectivity might be related with the functional group such C = O in ACNFs as presented in FTIR results. The carboxyls group has stronger attraction with polar gas such as carbon dioxide that caused the solubility and gas permeability of CO₂ increased [11-12]

4.0 CONCLUSION

MMMs deriving from ACNF with different composition fabricated via dry/wet inversion technique. The SEM images obtained the cross-sectional area of the PSf/ACNF membranes indicated that ACNFs well dispersed in the PSf matrix at 0.1, and 1.5wt% ACNF loading. Based on the results, shown that the performance of the MMMs have relied on the precursor polymer composition. Furthermore, the PSf/ACNF MMMs selectivity and permeability increased slightly to create best composite membrane.

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