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Analysis of the influence of CMS variable percentages on pure PES membrane gas separation performance

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Abstract

Distinct percentages of carbon molecular sieve (CMS) were added to Polyethersulfone (PES) matrix to generate mixed matrix membranes (MMMs) using solution casting method. The characterization was conducted by thermogravimetric analysis (TGA) to find out the residue solvent in the membranes and field emission scanning electron microscopy (FESEM) analysis to check the morphology of membrane. TGA results demonstrated no remaining solvent and also FESEM images demonstrated acceptable bonds between the filler particles and the polymer chains. The gas permeation results divulged that both CO_2 permeance and CO_2/CH_4 selectivity went up with CMS loadings increment as compared to pure PES membrane. Obtained results revealed that the greatest value of CO_2 permeance (68 GPU) and CO_2/CH_4 selectivity (11.15) at a pressure of 8 bars can be accomplished with 15 wt. % loading of CMS particles. This can be related to the kinetic diameter of CMS particles that places between CO_2 and CH_4 kinetic diameters.

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Keywords: mixed matrix membrane; Polyethersulfone; gas separation; carbon molecular sieve

1. Introduction

The consumption of natural gas as a cleaner and more useful type of fuel has been increasing. Natural gas is also contemplated as the major feed for the chemical industry due to its rising global consumption [1]. In natural gas, there are a lot of impurities like acid gases. The most important impurity in natural gas is CO_2 which needs to be

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removed from it. Acid gases such as H_2S and CO_2 in natural gas have no heating value, and they generate acids or acidic solutions when in touch with water, which are all corrosive. CO_2 separation from natural gas is very crucial as it is one of the most typical and disruptive contaminants. Acid gases amount could reach and even go above 50% volume in some unconventional natural gas well streams [2-6]. In order to remove these impurities, there are different separation technologies like absorption, adsorption, cryogenic and etc. However, as an alternative, membrane separation technology has shown auspicious features and accordingly, attracted massive attention from the industry due to its energy efficiency, simple process design, ease of scale-up and module construction as well as economic advantages [7, 8]. Membrane systems have shown up to isolate acid gas from natural gas for the recent decades [9]. At the moment, separation of CO_2 from natural gas is the only membrane-based procedure carried out on an expansive extent; membrane is a thin layer which acts selectively between two fluids to separate them according to its properties and the targeted application. Membrane is categorized into two structures: dense or porous whereby dense membranes are completely uniform in composition and structure while porous ones may be chemically or physically heterogeneous in which pores or layered structures are formed. The mixed-matrix membrane (MMMs) is a novel category of membrane materials used for gas separation and have a very significant role in the development of current membrane-based separation technology. Mixed matrix membranes (MMMs) are usually composed of a porous or nonporous inorganic filler such as zeolites, nanosize TiO_2, SiO_2, MgO, MOF, Carbon molecular sieves (CMSs), carbon nanotubes or clay particles [10-13] dispersed in a continuous polymer matrix. MMM are generated with the aim of improving the separation performance of the polymeric membranes. Furthermore, the mixed matrix specifications are impacted by filler particle size, pore size, filler loading and polymer characteristics [14]. In a research work by Vu et al [15] carbon molecular sieves (CMSs) have been incorporated into two distinct polymer matrices to produce mixed matrix membranes for gas separation purposes, and enhancement in permeation properties in comparison with those of the pure polymeric membranes as well as significant improvements in both CO_2/CH_4 and O_2/N_2 selectivities, were detected. Carbon molecular sieve (CMS) is one of the molecular-sieve type of inorganic fillers incorporated in mixed matrix membranes (MMMs) and it is produced by the pyrolysis of thermosetting polymers having wide openings with limited pores [16]. Also, CMS particles can create strong interactions with glassy polymers [17]. In order to investigate the effects of CMS on a polymeric matrix like PES to get to know more about mixed matrix membranes, this study has been developed and explored the effects of CMS variable percentages (5, 10 and 15 wt.%) on the morphology and the CO_2/CH_4 gas separation performance of PES-CMS MMMs.

2. Materials and Methodology

2.1. Material

Polyethersulfone (PES) (ULTRASON E 6020P) having a molecular weight of 50,000 g/mol, was purchased from BASF Germany. N, N-Dimethylformamide (DMF) EMPLURA® got purchased from Merck Germany was used as solvent for the preparation of MMM solutions. The inorganic filler, CMS was purchased from Japan Enviro Chemical.

2.2. Synthesis of Mixed Matrix Membranes

The membranes were fabricated using the solution casting method. Before proceeding with the membrane fabrication, CMS particles and PES flakes were dried in oven at 100^{o}C for 2 hours to remove moisture. Different loadings of CMS from 5 to 15 wt.% were added to the pure polymer in order to synthesize mixed matrix membranes. Firstly, a particular portion of CMS was added to DMF and was stirred for a while and then the remaining CMS was added to the solution and stirred for 24 hours. After that PES was combined with the mixture gradually and again was stirred for another 24 hours and then ultrasonication was done for 30 mins to achieve a homogenous solution. The next step was to cast the accomplished solution by casting machine and then to dry it in the oven for 1 hour at 150^{o}C. The resulted mixed matrix membranes were characterized by using variable pressure

field emission scanning electron microscope (VPFESEM, Zeiss Supra55 VP) for morphology and Thermogravimetric Analysis (TGA) for weight loss analysis.

2.3. Gas Permeability Study

The produced mixed matrix membranes were tested for permeability of pure (99.99%) carbon dioxide (CO_2) and methane (CH_4) using gas permeation unit at room temperature (25°C) and pressure of 8 bars. The below equation was used for permeance calculation:

$$P_i/L = N_i/\Delta P_i \quad (1)$$

Where P is the permeability of the test gases, L is the thickness of the membrane, N is the gas flux through the membrane and ΔP is the pressure difference. The membrane selectivity (α) was calculated by following equation (Eq. (2)):

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

3. Results and Discussion

3.1. Thermal analysis of membranes

TGA test has been mainly conducted to determine the amount of residue solvent in the resulted membranes. The membranes were exposed to the same experimental conditions where they were heated from 30°C to 800°C at a rate of 10°C/min. Fig. 1 shows the weight loss of the produced membranes over the temperature range. As it can be seen, there are two thermal drops in all membranes` graphs; One is at around 155°C which is the evaporation temperature of the DMF solvent however this fall is not very steep demonstrating that the residue solvent in all fabricated mixed matrix membranes as well as the pure PES is less than 2% which is desirable. The second drop in the graphs is very drastic being seen at around 500°C which is the decomposition temperature of PES as the main phase in the membranes [18-20], so when it is degraded by temperature, a very dramatic fall is exhibited. CMS has increased the thermal stability of the pure PES membrane; as it can be observed in the graphs, by adding more CMS, the thermal stability of the membranes compared to the neat PES has risen [20].

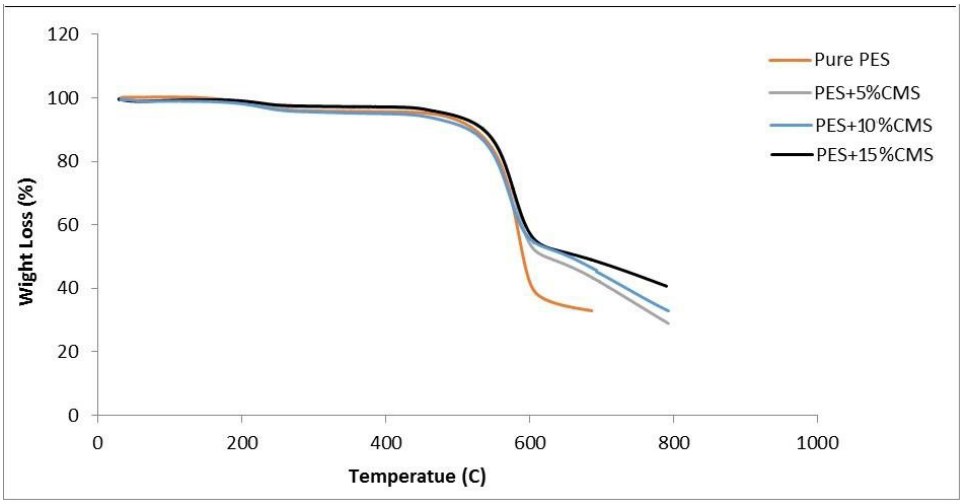
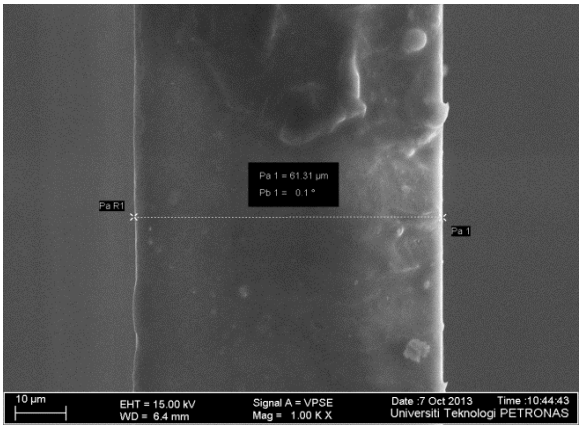


Fig 1. TGA Analysis for Pure PES Membranes, PES+5%CMS, PES+10%CMS, PES+15%CMS

3.2. Morphological analysis of membranes

MMMs including CMS were produced by solution casting approach. Field Emission Scanning Electron Microscopy (FESEM) was performed to check the cross section of the fabricated MMMs. Fig. 2 (a) shows the cross-section of the pure PES membrane. All the produced membranes emerged to have a dense structure according to FESEM images. Fig. 2 (b) and (c) illustrated the cross section of PES with CMS (5 wt.%) and CMS (10 wt.%) respectively. From the images, it can be observed that the backbone structure is very dense and smooth and also CMS particles have been dispersed very well all through the matrix phase without any agglomerations. Therefore, it shows that the interactions between the filler and the polymer was well enough to let the CMS particles distribute well throughout the membrane; this can be contributed to 48 hours continuous stirring followed by 30min ultrasonication which has resulted in a good CMS dispersion in PES. Moreover, the desirable interaction between CMS particles and polymer chain matrix is achieved as shown in Fig. 2 and further endorsed by the gas permeation outcomes [14]. Also, Vu et al. synthesized a mixed matrix membrane comprising of self pyrolyzed CMS as the inorganic filler and polyimide as the polymeric phase and recorded good interactions between polymer and CMS particles [15]. However, by increasing the filler load apparently a slight particle agglomeration will be observed because of the increasing interactions amidst the particles [21]. Some modification techniques were used to reduce this agglomeration such as efficient sonication.



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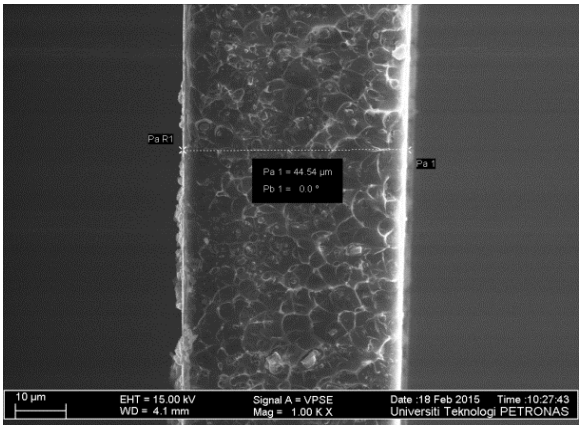

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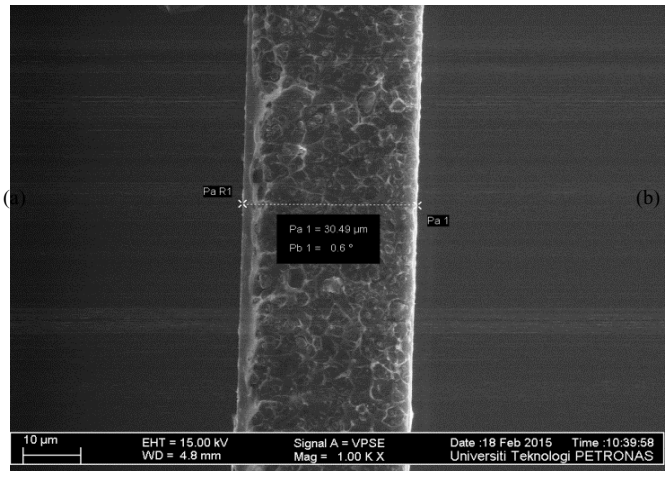
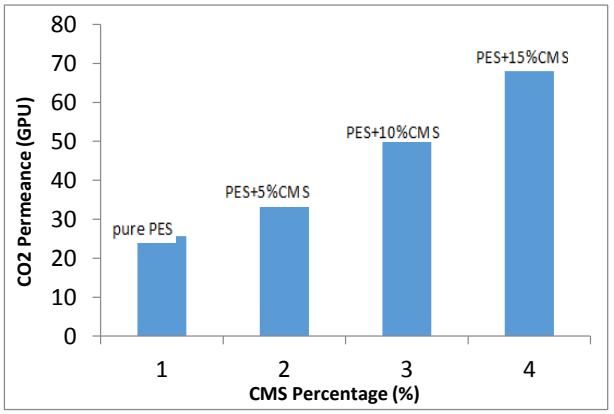


(c)

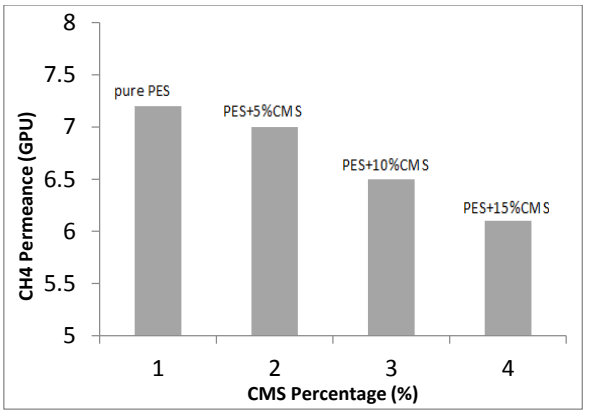
Fig 2. FESEM cross-sectional Images of (a) pure PES membrane, (b) PES+5%CMS, (c) PES+10%CMS

3.3. Gas Permeability Test

In order to investigate the membrane gas separation performance, pure gas permeation tests were conducted using pure CO_2 and pure CH_4 gases at a pressure of 8 bars. The gas permeance of CO_2 and CH_4 and also selectivity studies of CO_2 and CH_4 for pure PES membrane, and mixed matrix membranes are shown in Fig.3 (a), (b) and (c). It is discovered that the CO_2 permeance boosted with CMS content increment. However, CH_4 permeance has slightly decreased with increasing CMS percentage; this can be attributed to the kinetic diameter of CMS. The CO_2 kinetic diameter (3.3Å) is lower than that of CMS (3.8Å) while the CH_4 kinetic diameter (3.8Å) is approximately the same as kinetic diameter of CMS. Consequently, CMS particles were able to restrict CH_4 molecules from passing through the membrane [22, 23]. The obtained results also show that there is an increase of CO_2 gas permeance and ideal selectivity by adding CMS particles to pure PES membranes. As anticipated, the incorporation of CMS particles into pure PES increased the CO_2 permeance and CO_2/CH_4 selectivity of MMMs; these results are in good agreement with previous study as well [20]. The most remarkable increment in CO_2 permeance and CO_2/CH_4 selectivity was monitored at 15 wt.% amount of CMS. Comparing with the pure PES membrane, the CO_2 permeance inflated from 25.7 to 68 GPU and the CO_2/CH_4 selectivity rose from 3.57 to 11.15 at a pressure of 8 bars. Considering the accomplished results, it can be wrapped up that CMS particles interacts well with pure PES matrix which is in accordance with the outcomes reported by Vu et al. [15].



(a)



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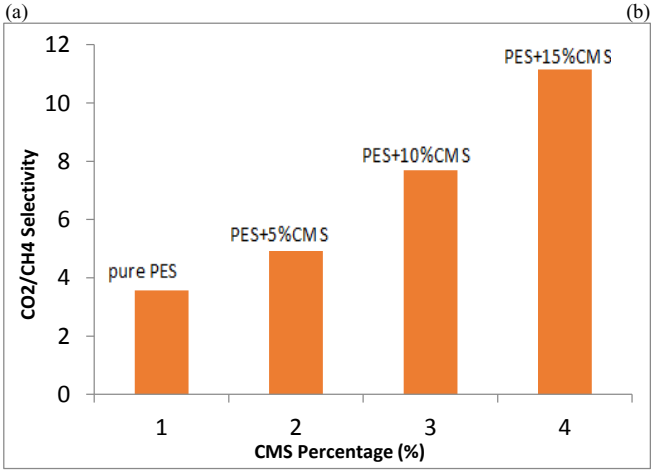

(c)

Fig 3. (a) permeance of CO_2, (b) Permeance of CH_4 and (c) CO_2/CH_4 Selectivity

4. Conclusions

Mixed matrix membranes of PES and CMS were fabricated. TGA results showed no residue solvent in the membranes so no blocking agent were there and gas molecules could pass through easily. A dense structure was obtained for all the membranes and also CMS particles were dispersed smoothly and homogenously throughout the matrix phase. This study showed that the addition of 15 wt.% CMS as inorganic filler to PES dope solution rose the CO_2 permeance and selectivity of CO_2/CH_4 gas mixture very drastically.

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