PVDF/PBI membrane incorporated with SAPO-34 zeolite for membrane gas absorption

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ABSTRACT

Polymeric membranes with low surface energy and large pore size are most desirable in membrane gas absorption (MGA). In this paper, PVDF membrane was incorporated with gas selective SAPO-34 zeolite and blended with hydrolytically stable polybenzimidazole (PBI) to engineer a membrane contactor with additional functionality and stability. The effects of inorganic fillers and PBI on the membranes properties and the CO_2 absorption performance were studied. In addition, the results were compared to PVDF membrane with PBI, modified and unmodified SAPO-34 zeolite. The hydrophilic SAPO-34 zeolite was modified into the hydrophobic SAPO-34 zeolite using fluorocarbon silane. The CO_2 flux of PVDF membrane increased 60% when it was blended with 10 wt% of SAPO-34. The presence of SAPO-34 in PVDF membrane enriched membrane porosity and affinity towards CO_2. The PVDF membrane with hydrophobic SAPO-34 exhibited a dense membrane structure, resulting in a great membrane resistance for CO_2 transfer. Although PVDF membrane with both PBI and SAPO-34 (P-5S34-5PBI) showed lower CO_2 flux than the PVDF membrane with SAPO-34 (P-10S34), the addition of 5 wt% of PBI provided better membrane stability in the corrosive solution.

1. Introduction

Biogas production has been globally promoted due to the need of renewable energy. In Malaysia, Federal Land Development Authority (FELDA) and Sime Darby Plantation Sdn. Bhd have initiated the generation of biogas as well. This is because that oil palm industry produced a huge amount of biomass wastes that contribute about 85.5% of the total biomass [1]. FELDA is currently having 12 biogas trapping plants [2], meanwhile Sime Darby Plantation is collaborating with Tenaga Nasional Berhad to develop 6 potential biogas plants [3]. Besides methane (CH_4), the biogas contains up to 60% of carbon dioxide (CO_2) [4]. The fuel gas efficiency is significantly reduced due to the presence of CO_2 [5]. Among the gas purification methods, membrane gas absorption (MGA) is the most appropriate technology for biogas upgrading as it requires a low pressure in CO_2 separation. MGA also shows other advantages such as small foot-print, easy scale-up and flexible modularity. More importantly, MGA exhibits the excellent mass transfer properties because it integrates the benefits of chemical absorption and membrane process [6].

Commonly used hydrophobic polymeric membranes in MGA are polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE) and polyvinylidenefluoride (PVDF) membranes. However, most of these polymeric membranes are not able to maintain their performance during MGA due to the property changes in amine solutions. PVDF showed poor resistance in diethanolamine (DEA) solution [7]. The defluorination of PVDF was postulated to be the primary reaction in amine solutions, causing the loss of surface hydrophobicity. In order to further improve and sustain the membrane hydrophobicity, surface modification by blending fluorinated surface modifying macromolecule (SMM) had been widely reported [8,9]. The migration of SMM to the air interface during phase inversion could enhance the surface properties without significant alterations on the physical properties of the base membrane. The blended membranes were also successfully tested in MGA for long operation period without obvious changes on the membrane properties. On the other hand, several researchers reported on the development of polymer membranes with the solvent resistance by introducing siloxane networks. Park et al. [10] successfully prepared electrospun PVDF/siloxane nanofibrous membranes with solvent resistance which is better than the pristine PVDF nanofibrous membranes. The incorporation of tetraethyl orthosilicate (TEOS) improves the solvent resistance and mechanical strength of nanofibers due to the formation of a siloxane

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network among PVDF chains. Lin et al. [11] modified the highly porous polyvinylidene fluoride (PVDF)/siloxane nanofibrous membrane using fluoroalkylsilane (FAS) and the membrane was successfully tested in MGA for 4 days. The blending of inorganic filler into polymeric matrix to form mixed matrix membrane (MMM) had also been widely reported by many membrane researchers, but these membranes were rarely tested in MGA. Recently, Zhang and Wang [6,12] reported the use of hydrophobic silica in the engineer of hydrophobic poyetherimide (PEI) membrane for MGA. In their earlier work [12], the fluorinated silica was prepared via one pot synthesis by simple mixing of TEOS and perfluorodecyltriethoxysilane (PFTS). The PEI membrane was modified using (3-aminopropy) trimethoxysilane (APTMS) and then immersed into the mixture of TEOS and PFTS to enhance the membrane surface roughness and hydrophobicity. Their later work [6] reported on a slightly different preparation route which only involves the fluorination after incorporating silica on PEI surface. The later method was favorable to generate a more uniform coverage of PFTS network on SiO_2. Both membranes showed stable flux of CO_2 in a long term operation of MGA using pure CO_2 as the feed. Ismail et al. [13] also reported on the use of hydrophobic clay to reduce the surface energy of PVDF membrane. The MMM showed increment on both CO_2 and N_2 permeances. The separation performance of these mixed matrix membranes in MGA using mixed gas was not reported.

Membrane contactor should be designed with special character to enhance CO_2 absorption in MGA. The membrane contactor could be further functionalized by incorporating filler with gas selectivity. Compared to other porous materials, small pore zeolites especially SAPO-34 appears to be interesting due to its high adsorption affinity to CO_2. SAPO-34 zeolite is a chabazite (CHA) structure zeolite with a framework pore size of 0.38 nm, which is similar to the molecule sizes gases in a biogas mixture. Researchers highlighted the capabilities of zeolite to enhance the gas separation of membrane many times in their works [14–16]. The addition of zeolite into polymeric membranes increased the CO_2 permeance about tenfold and improved the gas selectivities (CO_2/N_2 and CO_2/CH_4) more than 35% [14,17]. Besides the gas separation performance, the incorporation of zeolite also improved the thermal stability of MMMs as depicted by an increment of the glass transition temperature (T_g) [16]. Furthermore, the fluorinated SAPO-34 could be added into membrane to study the effects of filler hydrophobicity on the membrane characteristics and performance. The stability of mixed matrix membrane should be further improved by blending polybenzimidazole (PBI). PBI blended polymer showed outstanding chemical resistance, thermal stability and strength over the common polymers as reported by others [18–20]. SAPO-34 and PBI have excellent features to be used as the additives in MMMs for MGA applications, but such study has not been reported in the literature to our best knowledge. In this paper, PVDF mixed matrix membranes were engineered with SAPO-34 zeolite and PBI to enhance their characteristics and separation performances in MGA. The MMMs were characterized and tested in MGA for CO_2 absorption.

2. Experimental

2.1. Membrane preparation

PVDF from Solef Company (Solef 6010/1001) was used as the basic polymer to prepare the membranes while n-methyl-2-pyrrolidone (NMP) (Emplura, Merck Chemical) was used as the solvent. In this study, membrane was prepared using two-stage soft coagulation baths system [21]. A mixture of NMP in water and ethanol (absolute for analysis, Merck Chemical, Malaysia) were used as the coagulants. The polymer solution was cast on glass plate using a blade with a gap of 40 μm. The wet polymer film

Table 1
Description of membrane compositions.

Composition	Membrane				
(wt. %)	P0	P-10S34	P-10MS34	P-10PBI	P-5S34-5PBI
PVDF	15	13.5	13.5	13.5	13.5
NMP	85	85	85	85	85
Additive	0	1.5 (SAPO-34)	1.5 (Modified SAPO-34)	1.5 (PBI)	0.75/0.75 (PBI/SAPO-34)

was directly immersed into pure ethanol for an hour and followed another an hour in 80 wt% of NMP in water. Then, the wet polymer film was immersed into water for few hours to remove residual chemicals and dried at ambient temperature.

SAPO-34 was prepared using a mixture of Al_2O_3: P_2O_5: $0.6SiO_2$: 1.07 TEAOH: 56 H_2O as reported by other [22]. (Heptadecafluoro1,1,2,2-tetrahydrodecyl) triethoxysilane (FAS, Gulf Chemical Pte. Ltd., Singapore) was used to fluorinate the SAPO-34. A mixture of 1 ml FAS in 50 ml of ethanol was used to modify SAPO-34 zeolite. SAPO-34 zeolite (3 g) was reacted with FAS solution for an hour and rinsed with ethanol to remove the excessed FAS. The modified SAPO-34 was dried in an oven before blending into membrane.

The modified and unmodified SAPO-34 were added into NMP separately and stirred for 30 min. Polybenzimidazole (PBI) (Celazole ® T-Series) was mixed with NMP and stirred vigorously in at 150 °C for 24 h. The PBI polymer solution was cold down at ambient temperature and then centrifuged for 5 min at 3500 rpm to remove remaining PBI particles. PBI polymer and SAPO-34 solutions were sonicated for 30 min. Then, 10 wt% of PVDF was added into the solution with SAPO-34 and/or PBI polymer for 12 h at 40 °C. After that, the mixture was sonicated for another half an hour before adding the remaining PVDF. The polymer solution was stirred for 2 days and ultrasonic for 30 min before membrane casting. The membrane composition is summarized in Table 1.

2.2. Membrane characterization

The water contact angle on PVDF membranes were measured using a goniometer (Ramé-Hart Instruments Co.). In the measurements, deionized water was dropped at different points on the membrane samples to obtain an average contact angle values. The water contact angle on the fresh membranes and the membranes immersed in 0.2 M of DEA for 2 h were measured. A scanning electron microscopy (SEM, Hitachi, TM3000) and an atomic force microscopy (AFM, Park System, XE-100) were used to observe the membrane morphology and topology. All the membrane samples were coated with platinum to obtain the clear SEM images by avoiding charge accumulation on the membrane samples. The membrane samples were fractured in liquid nitrogen for the cross-sectional views. Some edible oil with a density of 906.044 g/L was used for the membrane porosity test. The membrane porosity was calculated as shown below

$$\%Porosity, \phi = \frac{\text{Volume of in membrane (Voil)}}{\text{Total volume of membrane (vmemrane)}} x \ 100\%$$

(1)

On the other hand, the chemical difference of the membrane samples were studied using a Fourier Transform Infrared spectrometer (FTIR) (Nicolet iS10,Thermo Scientific, USA). The membrane thicknesses were measured using a digital micrometer. In addition, a porometer (Porolux 1000) was used to measure membrane pore size. The membrane samples were immersed into Porofile (16 mN/m surface tension) wetting liquid for an hour before pore size measurement.