



Amine wetting evaluation on hydrophobic silane modified polyvinylidene fluoride/silicoaluminophosphate zeolite membrane for membrane gas absorption

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ARTICLE INFO

Keywords:

Membrane gas absorption
Carbon dioxide
Membrane wetting
Silane modification

ABSTRACT

Membrane wetting in membrane gas absorption is undesirable as it reduces the gas transfer in wet pores. This work aims to understand the improvement of membrane hydrophobicity using fluoroalkyl silane and its effects on membrane properties, separation performance and membrane wetting by amine. Polyvinylidene fluoride/silicoaluminophosphate zeolite membranes were prepared using non-solvent induced phase separation technique and then immersed into a mixture of (3,3,3-trifluoropropyl) trimethoxysilane and ethanol solution (volume ratio of 1: 100) for 20 min. The post-modification resulted in a slight improvement of water contact angle and liquid entry pressure. Hence, the highest CO₂ absorption flux of $4.48 \pm 0.36 \times 10^{-4} \text{ mol.m}^{-2} \cdot \text{s}^{-1}$ was achieved using silanated membrane, about 25 % of improvement in comparison to the neat membrane. The absorption flux of humid gas was slightly reduced (-16 %) due to pore wetting. Fluoroalkyl silane could be used to prevent water wetting, resulting improvement of CO₂ absorption. The membranes were immersed in diethanolamine solution (2 M) for 50 h before characterization using goniometer, Fourier transform infrared spectroscopy and scanning electron microscope. The incorporation of zeolite reduced membrane wetting because membrane swelling could be prevented. The unfavorable interaction between fluoroalkyl and amine groups induced severe membrane wetting by amine.

1. Introduction

Amine dominates the market up to 90 % of CO₂ capture of for the absorption systems (Zhao et al., 2016). Besides blending different types of absorbent (Li and Zhang, 2018; Li and Zhang et al., 2018), the cost and absorber size can be greatly reduced using a macroporous membrane which provides a large surface area to transfer CO₂ into the absorbent circulated at the other side of membrane. Although the field tests of membrane gas absorption in many countries have shown positive results, (Falk-Pedersen and Dannström, 1997; Feron and Jansen, 1995; Scholes et al., 2014; Li et al., 2013), the tested membrane gas absorption systems have not been commercialized up to date due to the concerns on membrane wetting for long operations. Membrane wetting is a condition where the membrane pores are filled up with liquid hence cause serious reduction of CO₂ transportation.

Hydrophobic polymers including polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polypropylene (PP), poly (ether ether ketone) (PEEK) and more had been widely used to develop the hydrophobic membranes with minimum wetting to achieve a high mass

transfer rate through air-filled pores. Besides conventional pore formers such as phosphoric acid, glycerol, polyethylene glycol (PEG) and lithium chloride (LiCl), different types of inorganic particles including montmorillonite (Rezaei et al., 2015), zeolite socony mobil-5 (ZSM-5) (Shirzadeh-Gharacheh and Rahbari-Sisakht, 2016), hydrophobic CaCO₃ (Fosi-Kofal et al., 2016), graphene (Wu et al., 2016), polyhedral oligomeric silsesquioxane (POSS) (Ahmad et al., 2017) and silico-aluminophosphate-34 (SAPO-34) zeolite (Ahmad et al., 2016b) were blended into hydrophobic polymers to improve membrane properties such as surface hydrophobicity, porosity, pore size and gas affinity. These mixed matrix membranes could be further modified using hydrophobic silane in order to achieve superhydrophobicity (Hamzah and Leo, 2016). In the past, researchers had tried different methods to improve membrane hydrophobicity up to superhydrophobic state in the combat of membrane wetting. A thin layer of porous polyethylene (low density) was coated on poly (vinylidene fluoride) (PVDF) hollow fibers to create superhydrophobic surface (Ahmad et al., 2013). The coated PVDF membrane exhibited an improved CO₂ flux in membrane gas absorption compared to the neat PVDF hollow fibers. On the other hand,

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<https://doi.org/10.1016/j.jngse.2018.08.003>

Received 13 June 2018; Received in revised form 20 July 2018; Accepted 14 August 2018

Available online 18 August 2018

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Table 1
Composition of polymer solution to prepare PVDF and PVDF/SAPO-34 membranes.

Composition (wt%)	Membrane		
	P-0	P-5S34	P-10S34
PVDF	15	14.25	13.50
NMP	85.00	85.00	77.00
SAPO-34	0.00	0.75	1.50
Silane modified membrane	P-0F	P-5S34F	P-10S34F

superhydrophobic polyether ether ketone (PEEK) hollow fibers were produced by chemical modification of PEEK hollow fibers using a functional perfluoro oligomer (Li et al., 2013). Superhydrophobic ceramic membranes were also applied in membrane gas absorption (Abdulhameed et al., 2017; Yu et al., 2015; An et al., 2015). Different types of fluoroalkyl silane were used to convert these hydrophilic ceramic membrane into superhydrophobic membranes. Although silane grafting increased the mass transfer resistance of ceramic membranes slightly, the superhydrophobic ceramic membranes were less fouled by the dust in flue gas in comparison to PP membrane. However, periodic drying was still practiced during the field test of superhydrophobic membrane in order to reduce membrane wetting (An et al., 2015).

Before conducting more research on membrane gas absorption using membranes with various types of hydrophobic enhancement, it is important to understand the wetting mechanisms. Several groups of researchers concluded that the wetting of PP and PVDF membrane was actually triggered by absorbent diffusion and membrane swelling (Lv et al., 2010; Mahmud et al., 2004). The effects of hydrophobicity improvement on membrane wetting in amine absorbent remains unclear since most the wetting evaluation usually involves water contact angle measurement on the fresh membranes only without further details (Ahmad et al., 2010, 2012). The improvement of CO₂ flux within the short operation duration could be related to morphology improvement instead of wetting reduction. In this work, the major aim is to study the modification effects of hydrophobic silane on the mixed matrix membrane used in membrane gas absorption. PVDF/SAPO-34 membrane developed in our previous work (Ahmad et al., 2016b) was modified using fluoroalkyl silane to improve membrane hydrophobicity. The membranes were further characterized and tested to understand the effects of silane. The membranes with hydrophobic enhancement were also evaluated in amine wetting test. This test is helpful to generate some preliminary knowledge regarding the effects of hydrophobicity enhancement on membrane wetting by amine.

2. Materials and methods

2.1. Membrane preparation

The hydrophobic and macroporous PVDF and PVDF/SAPO-34 membranes were prepared using non-solvent induced phase separation (NIPS) method. SAPO-34 zeolite was first hydrothermally synthesized based on the previous work (Junaidi et al., 2014). SAPO-34 zeolite particles were further dispersed in the solvent, *N*-methyl-2-pyrrolidone

Table 2
Characteristics of PVDF, PVDF/SAPO-34 and post-modified membranes.

Membrane	Water contact angle (°)	Surface roughness, R _a (μm)	LEP (bar)	Mean pore size (nm)	Thickness (μm)	Porosity (%)
P-0	141.1 ± 1.2	1.105	0.903 ± 0.012	812.29 ± 56.65	158 ± 23	71.5
*P-0F	140.5 ± 2.2	0.872	0.979 ± 0.084	726.13 ± 37.92	156 ± 6	71.2
P-5S34	122.9 ± 2.5	0.742	2.313 ± 0.023	312.61 ± 7.39	132 ± 6	66.0
*P-5S34F	129.2 ± 2.0	0.612	2.527 ± 0.103	300.24 ± 9.53	121 ± 5	64.4
P-10S34	121.6 ± 4.1	0.600	0.928 ± 0.079	800.59 ± 40.46	111 ± 6	51.3
*P-10S34F	124.3 ± 6.6	0.507	0.959 ± 0.013	804.41 ± 16.56	115 ± 4	50.2

(NMP) (Emplura, Merck Chemical) under sonication (Ahmad et al., 2016b). In order to achieve a homogeneous solution, PVDF powder (Solef® PVDF 6010/1001) was dried at 60 °C before it was slowly dissolved into the solvent at 40 °C as described in previous work (Ahmad et al., 2017). Then, the mixture was continuously stirred at 40 °C for another 24 h. The polymer solution was cast on a glass plate using a casting machine (Elcometer 4340, United Kingdom) with a casting gap of 400 μm. The wet polymer films were instantaneously immersed into a coagulation bath containing 100 wt% of ethanol (ethanol absolute for analysis, Merck) for one hour and, followed by the second bath for one hour containing 80 wt% of NMP and 20 wt% of water. The membrane was finally immersed into water to remove the chemical residues. The zeolite loading in polymer solution was varied at 0 wt%, 5 wt% and 10 wt% based on the polymer content as summarized in Table 1. The membrane samples were labelled as P-0, P-5S34 and P-10S34 based on the zeolite loading.

All the membrane samples were dried in an oven at 60 °C for 24 h before silane modification. The hydrophobic silane ((3,3,3-trifluoropropyl) trimethoxysilane, Gelest, Inc., Morrisville) was mixed with ethanol at a volume ratio of 1:100 to form silane solution. The silane solution was stirred for 1 h at ambient temperature before immersing the membrane samples for 20 min. The modified membranes were dried in the oven at 60 °C for 24 h and they were labelled as P-0F, P-5S34F and P-10S34F, respectively.

2.2. Membrane characterization

Membrane hydrophobicity was evaluated in term of water contact angle measured using a goniometer (Ramé-Hart Instruments Co.). Distilled water was dropped at few locations on the membrane surface to obtain an average water contact angle. Meanwhile, liquid entry pressure (LEP) and pore size were measured using a porometer (Porolux 1000). Distilled water was used in the LEP measurement, while Porefil (surface tension of 16 mN/m; density of 1.8695 g/cm³) was used to wet the membrane samples for 1 h before the pore size measurement. On the other hand, Membrane porosity was determined using gravimetric method as described below by equation (Ahmad et al., 2016b).

$$\text{Porosity (\%)} = \frac{V_{\text{porefil}}}{V_{\text{membrane}}} \times 100 \quad (1)$$

where V_{membrane} is the volume of membrane sample (cm³) and V_{porefil} is the volume of Porefil solution absorbed by membrane sample (cm³). A thickness gauge (Mitutoyo Thickness Gage, 547-400S EA) was used to measure the membrane thickness for volume calculation. Furthermore, the membrane morphology was studied using a scanning electron microscopy (SEM, Hitachi, TM3000). The membrane samples were fractured in liquid nitrogen to obtain the cross-sectional view. An atomic force microscopy (AFM, Park System, XE-100) was used to study the surface morphology and topology of membranes. The chemical changes on the membrane samples due to silane modification were also studied using a fourier transform infrared (FTIR) spectroscopy (Nicolet iS10, Thermo Scientific).

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