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Preparation and characterization of PVDF-montmorillonite mixed matrix hollow fiber membrane for gas–liquid contacting process

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ABSTRACT

Porous PVDF-hydrophobic montmorillonite (MMT) mixed matrix membranes (MMMs) were fabricated via wet spinning method and used in membrane gas absorption process. The effects of hydrophobic MMT nano-clay loadings (1, 3 and 5 wt% of polymer) on the structure and performance were investigated. The fabricated membranes showed both finger-like and sponge-like structure with an increase in the length of finger-like pores in their cross-section, which resulted in higher permeability and lower mass transfer resistance compared to plain PVDF membrane. Also, significant improvements for surface hydrophobicity, critical entry pressure of water and porosity with the addition of filler were observed. The CO_2 absorption test was conducted through the gas–liquid membrane contactor and demonstrated a significant improvement in the CO_2 flux with MMT loading and the membrane with 5 wt% MMT presented highest performance. For example, at the liquid water velocity of $0.5\,m\,s^{-1}$, CO_2 flux of the MMM with 5 wt% MMT of $9.73 \times 10^{-4}\,mol\,m^{-2}\,s^{-1}$ was approximately 56% higher than the PVDF membrane without nano-filler. In conclusion, MMMs with improved absorption properties can be a promising candidate for CO_2 absorption and separation processes through membrane contactors.

Keywords: Carbon dioxide absorption; Mixed matrix membrane contactor; Morphology; Hydrophobicity; Permeability; Montmorillonite nano-clay

1. Introduction

Threatening levels of anthropogenic greenhouse gases, particularly carbon dioxide (CO_2), pose great environmental, economic and operational impacts to the Earth. Hence, the reduction of CO_2 content in gas streams and its emission to the atmosphere seems inevitable. Industrial methods of CO_2 capture by means of direct contact between gas and liquid in physical or chemical absorption processes through packed or tray towers are widespread. However, these methods face some problems such as low contact area, tremendous energy consumption, and may result in operational drawbacks such as weeping, foaming and flooding (Luis et al., 2011; Riemer, 1996; Xu et al., 2008).

Membrane contactors, which are designed to absorb CO_2, are newly devised apparatus with a solid, microporous and hydrophobic membrane. Membrane contactors have drawn considerable attention due to superior characteristics compared to conventional methods. Their advantages include high interface area per unit contactor volume, independent control of gas and liquid flow rates, small in size and easy to scale up and down (Drioli

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Nomenclature

A	contact area (m^2)
C_1	solute gas concentration in liquid ($mol\,m^{-3}$)
C_g	solute gas concentration in gas ($mol\,m^{-3}$)
ΔC_1^{av}	logarithmic mean of the difference in the concentration of solute gas in liquid phase ($mol\,m^{-3}$)
d_p	pore diameter (m)
d_i	inner diameter of hollow fiber (m)
d_o	outer diameter of hollow fiber (m)
d_{1m}	log mean diameter (m)
Gz	Graetz number, dimensionless
H	Henry's constant
Jav	average absorption flux ($mol\,m^2\,s^{-1}$)
K_{OL}	overall mass transfer coefficient ($m\,s^{-1}$)
k_L	liquid side mass transfer coefficient ($m\,s^{-1}$)
k_g	gas side mass transfer coefficient ($m\,s^{-1}$)
k_m	membrane mass transfer coefficient ($m\,s^{-1}$)
L	hollow fiber membrane length (m)
L_p	effective pore length (m)
M	molecular weight ($g\,mol^{-1}$)
m	distribution factor
p	pressure (pa)
$\bar{p}$	mean pressure (Pa)
$\bar{P}$	total gas permeance ($mol\,m^{-2}$)
P_p	gas permeance by Poiseuille flow regime ($mol\,m^{-2}\,Pa^{-1}\,s^{-1}$)
P_K	gas permeance by Knudsen flow regime ($mol\,m^{-2}\,Pa^{-1}\,s^{-1}$)
Q_L	liquid flow rate (m^{-1})
r_p	pore radius (m)
$r_{p,m}$	mean pore radius (m)
R	universal gas constant (8.314 $J\,mol^{-1}\,K^{-1}$)
Sh	Sherwood number, dimensionless
T	temperature (K)
V_{liquid}	liquid velocity in lumen side ($m\,s^{-1}$)
ζ	effective surface porosity
θ	contact angle of liquid and surface
μ	gas viscosity (Pa s)

et al., 2005; Ismail and Mansourizadeh, 2010). The gas transport in membrane contactor is based on a diffusion mechanism that allows the gas to flow from one end of the pore in contact with the gas to the gas/liquid interface at the other end of the pore (Mulder, 1996). Therefore, the membrane must have high hydrophobicity with small pore size to prevent wetting and high permeability to increase diffusion rate (Ismail and Mansourizadeh, 2010; Rangwala, 1996). Hence, there is a need to carefully choose the membrane materials to prepare membranes with improved structure to fulfill the requirements of gas/liquid contacting processes.

Those conventional polymeric materials of high hydrophobicity such as polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE), and polyvinylidene fluoride (PVDF) are polymeric materials favorable to fabricate porous hydrophobic hollow fiber membranes for gas absorption application. Over the past two decades, PTFE and PP polymers have been used as the only commercial symmetrical hollow fiber membrane contactor materials (deMontigny et al., 2006; Li and Chen, 2005; Li et al., 2008). However, these two materials have high crystallinity and are insoluble in common solvents under ambient temperature. Therefore, membranes should be fabricated via melting and stretching methods which generally provide symmetric structure with relatively low porosity and large pore size (Li and Chen, 2005). Among the above mentioned hydrophobic polymers, PVDF is preferred due to its high solubility in organic solvents and ease of conversion to asymmetric membranes via phase inversion method (Ismail and Mansourizadeh, 2010). It should be noted that among different methods used for membrane fabrication, the phase inversion method seems to be the most flexible technique since it permits excellent control on the pore size, porosity and pore size distribution (Ismail and Mansourizadeh, 2010; Jeon et al., 2008; Khayet et al., 2002; Yeow et al., 2004).

Polymeric membrane contactors are not free of drawbacks. For instance, the presence of membrane acts as an additional mass transfer resistance; even a small partial pore wetting can reduce the performance significantly (Mavroudi et al., 2006). Wang et al. (2005) reported an almost 20% reduction in performance when the membrane pores were only 5% wet. The feasible methods to prevent membrane pore wetting are using hydrophobic membranes, membrane surface modification, fabrication of membranes with denser top layer, selection of proper liquid absorbents and optimizing operation conditions (Li and Chen, 2005). Among these methods, selection of liquids with suitable surface tension and optimizing operation conditions are relatively operable. Lisitsin et al. (2008) solved this problem by preparing well-tailored membranes with high critical entry pressure of water (CEPw), hydrophobicity and small pore size. However, reducing pore size may lead to a decrease in membrane surface porosity, consequently resulting lower permeation flux (Mansourizadeh and Ismail, 2012). Therefore, the membranes should be carefully designed to make a trade-off between pore size and porosity. Membrane surface modification aiming to increase surface hydrophobicity with sufficient pore size and porosity deserves further consideration by means of astute selection of sufficiently high hydrophobic membrane precursor materials and closely examined membrane morphology (Atchariyawut et al., 2006).

Polymer–inorganic membranes, known as mixed matrix membranes (MMMs) are alternative materials that can be used to combat the limitations of polymeric membranes. MMMs combine the advantages of both membranes including high permeability, selectivity, hydrophobicity and mechanical stability (Drioli et al., 2011; Hashemifard et al., 2011; Husain and Koros, 2007; Sridhar et al., 2007). Picard et al. (2007) found nanocomposite membranes can exhibit superior barrier properties to gas and water than fabricated neat membrane. To obtain excellent MMMs properties, several important parameters including the size of the filler particles, the degree of dispersion in the matrix, and the degree of adhesion with the polymer matrix have to be taken into account during the fabrication process (Aroon et al., 2010; Goh et al., 2010).

Over the past couple of decades, clay particles have received considerable attention not only as fillers in ceramics, paint, rubber, paper and plastics, but also for the fabrication of MMMs (Hwang et al., 2011; Wang et al., 2009). Although, clay particles for applying in gas/liquid contacting process should be organically modified in order to render the surface of the clay toward hydrophobicity and enhance the adhesion between the hydrophobic polymers and the clay (Alexandre and Dubois, 2000; Giannelis, 1998; LeBaron et al., 1999). Hydrophobic surface modified MMT nanoclay is selected as it can reinforce mechanical strength and enhance physical

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