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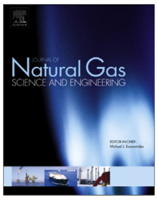

Study of CO_2 separation with PVC/Pebax composite membrane

Ehsan Ahmadpour [a], Ahmad Arabi Shamsabadi [a, b], Reza Mosayyebi Behbahani [a, *], Masoud Aghajani [a], Ali Kargari [c]

[a] Gas Engineering Department, Petroleum University of Technology, Ahwaz, Iran
[b] Marun Petrochemical Company, Mahshahr, Iran
[c] Membrane Processes Research Laboratory (MPRL), Department of Petrochemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Mahshahr Campus, Mahshahr, Iran

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ABSTRACT

Separation of CO_2 from CH_4 is a part of gas sweetening process for natural gas treatment. In the present study, Poly (amide − 6 − b − ethylene oxide) (Pebax MH 1657) copolymer was used as a selective layer to prepare PVC/Pebax composite membrane for CO_2 capturing. Gas permeation and transport characteristics of single and mixed gases for CO_2 and CH_4 were investigated and analyzed using constant pressure method. Trans-membrane pressure and temperature were varied from 5 to 15 bar and 20–50 °C respectively. The temperature dependency of selectivity for CO_2/CH_4 was decreased noticeably with an increase in temperature, whereas the permeability of both gases increased dramatically. Furthermore, the enhancement of CO_2 permeability with increase in gas pressure was probably due to the plasticization of membrane caused by relatively high solubility of CO_2 in the membrane. Mixed gases experiments were conducted with different concentration of CO_2 at constant temperature and pressure. Permeation measurement showed a steep decline on the membrane selectivity as the partial pressure of CO_2 decreased.

1. Introduction

The separation of polar gases like CO_2 from non-polar gases is an environmental and industrial importance (Thambimuthu et al., 2005), which is always desirable for decrease in concentration of greenhouse gases and prevention of acid rain formation. Moreover, the presence of CO_2 in the natural gas causes reduction of the heating value and waste of pipeline capacity (Mokhatab et al., 2006). Current technologies employed for the separation of CO_2 are mainly absorption (amines), adsorption and cryogenic distillation (Mokhatab et al., 2006). Membrane technology offers several advantages in comparison with other techniques, such as low-maintenance operations, low energy requirement, ease of scale-up, and exceptional reliability (Baker et al., 2004).

Polymeric membranes have been accounted as a viable technique for gas separation industries and serving as competitive candidate for traditional separation processes (Koros, 2010). Although, a major drawback of polymeric membranes has been the naturally counteracting permeability and selectivity (Rahman et al., 2013). Over the last few decades, many researchers have been working on various polymeric materials such as cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates, and polyetherimide for the preparation of gas separation membranes (Yampolskii, 2012). Poly(ether block amide) (Pebax) is a copolymer, composed of polyamide (PA) as hard segments and polyether (PE) as soft segments in the polymer chains (Joseph and Flesher, 1986). Usually, the hard blocks form frame structure and provide mechanical support, while the soft blocks with large free volumes are mainly for the transport channels. Pebax copolymer has been found to be a promising membrane material for the capture of polar gases as it has high polar gas permeability and high selectivity for polar gas/nonpolar gas mixtures (Ren, 2012).

Permeation of gases in membranes is a rate-controlled process that a high permeation could be achieved by using thin membranes (Liu et al., 2004). Structurally asymmetric and composite membranes with a thin selective layer and a porous substrate support are preferred for gas separation purposes. Asymmetric membranes with acceptable mechanical strength are hardly to be prepared from rubbery polymers thus the thin-film composite membranes are preferred (Blume and Pmnau, 1990). The latter can be prepared by coating or dip coating, which a suitable porous substrate with a

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* Corresponding author. Tel.: +98 6115550868.
E-mail addresses: r_behbahani@yahoo.com, rezabehbahani93@gmail.com (R.M. Behbahani).

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thin layer of the polymer that acts as the selective layer for separation. Recently, some researches are focusing on the improvement of selectivity and permeability of Pebax copolymer membranes by blending with other materials (Kim and Lee, 2001; Reijerkerk et al., 2010; Car et al., 2008a,b) or physical mixing with nanoparticles (Rahman et al., 2013; Li et al., 2013; SuryaMurali et al., 2010, 2014). For practical applications, the preparation of defect-free thin composite membranes with a Pebax selective layer is very important. In order to achieve this purpose some polymers like Polyetherimide (PEI) (Ren et al., 2012; Xiaoling et al., 2013), Polysulfone (PSf) (Liu et al., 2004), Polyethersulfone (PES) (SuryaMurali et al., 2010, 2014), Polyacrylonitrile (PAN) (Li et al., 2013; Le et al., 2011; Car et al., 2008a,b) and Polyvinylidene fluoride (PVDF) (Sridhar et al., 2007) has been used recently as porous substrate for composite membrane.

In this research, Poly (amide − 6 − b − ethylene oxide) (Pebax MH 1657) copolymer, composed of 60 wt.% of PEO and 40 wt.% of PA6 (nylon-6), was used to prepare flat sheet membrane and PVC/Pebax 1657 composite membrane for CO_2 separation. Gas permeation and transport characteristics of single and mixed gases (CO_2, CH_4) were investigated and analyzed using constant pressure method. Trans-membrane pressure and temperature were changed from 5 to 20 bar and 20–50 °C respectively.

2. Experimental

2.1. Material

Pebax® MH 1657 was purchased from ARKEMA (The Netherlands), is a polyether-block-amide composing 60 wt.% poly(ethylene glycol) (PEG) and 40 wt.% aliphatic polyamide (PA6, nylon6) and will be further referred to as 'Pebax1657'.The PVC was supplied from Abadan Petrochemical Company, Iran. The solvents—ethanol (99.9 wt%) and Dimethylformamide (DMF) were bought from Merck, Germany. Deionized water (conductivity less than 0.1 μS/cm) was obtained from Ramin power plant, Iran. All these chemicals were used as received. Both CO_2 and CH_4 used in the permeation experiments had purity of 99.999% and were acquired from Persian Industrial Gases, Iran.

2.2. Preparation of Pebax 1657 dense film

Firstly, Pebax 1657 copolymer was dried in an oven at 100 °C for 1 day. Then Pebax 1657 solution with a concentration of 3 wt. % was prepared with dried Pebax 1657 and solvent mixture of 70% ethanol and 30% w/w water. The polymer dissolved on a hot plate with surface temperature of 140 °C and rigorous stirring while maintaining under constant reflux over a period of 8 h. A solution casting method was used to prepare the dense film after gas bubbles removed. So the solution was poured in to a Petri dish and dried in oven for 2 days at 40 °C. The resultant dense flat-sheet membrane had a thickness of around 60 μm measured by a Mitutoyo micrometer.

2.3. Preparation of PVC/Pebax 1657 composite membranes

PVC microporous substrate was prepared by the phase inversion method (Arabi Shamsabadi et al., 2013a,b, 2014). A homogeneous solution of 15% w/w PVC in dimethyl formamide (DMF) solvent was cast on a nonwoven polyester fabric which was affixed on a glass plate. After casting, the glass plate was immediately immersed in distilled water bath at room temperature for 2h and then dried at room temperature for 1day. Ultraporous PVC substrates with 150–200 μm thickness were obtained. The PVC/Pebax composite membrane was obtained by coating the 3%wt. solution on PVC substrate for 4 times in period of 30min where between each periods the membrane was placed in oven at 40 °C. For extra vaporization of solvent the obtained composite membrane was placed in oven at 40 °C for 2 days. The thickness of membrane was determined by micrometer which was about 20 μm.

2.4. Gas permeability studies

Schematic diagram of the experimental setup is shown in Fig. 1. Gas inlet and outlet ports were provided in the test cell for the transport of feed, permeate, and retentate streams. The test cell contained a rectangular (4 cm × 5 cm) perforated plate affixed with a mesh to support a membrane of effective area 20 cm^2. Feed, permeate, and retentate lines were made of 1/4 in stainless steel (SS) 316 tubes. Feed gas flow rates are controlled by mass flow controllers. The experimental setup is flexible for testing membranes with both pure gases and mixed gases.

Pure gas experiments were carried out with pure CO_2, CH_4. Residual air present in the test cell, feed and retentate lines were flushed with the feed gas. The fluxes of the membranes were measured over a pressure range of 5–15 bar and temperature range of 20–50 °C. Feed gas was transported into the test cell with the outlet valve kept fully closed until the gauge specify the required pressure. After attaining the steady state, flow rate of permeate was calculated by utilizing a bubble flow meter. The gas permeability and the intrinsic selectivity were tested, which can be determined by Equations. (1) and (2)

$$P = \frac{Q.l}{A(p_2 - p_1)} \tag{1}$$

$$\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \tag{2}$$

where Q is the volumetric permeate gas flow rate ((cm^3 (STP)/s)), l is selective layer thickness (cm), A the effective membrane area (cm^2) for gas permeation, p_1 and p_2 are the feed side and permeate side pressures (cmHg), respectively. The unit of permeability was denoted as Barrer [1 Barrer $= 10^{-10}$(cm^3(STP) cm/cm^2 s cmHg)]. All the gas permeation experiments were performed more than four times and the reported values were the mean of at least four experiments.

Single gas transport properties are more often reported than gas mixture data. In most cases ideal gas selectivities are higher than mixed gas selectivities. However, it is well known that only experiments with gas mixture can show and estimate the applicability and feasibility of membranes to separate a target gas mixture. CO_2 mixed gas separation experiments were conducted using a 90/10 vol.%, 75/25 vol.% and 50/50 vol.% CH_4/CO_2. The permeation test was conducted at 5 bar and 25 °C. The feed and permeate compositions were analyzed using an YL Instrument gas chromatograph (GC). The Permeability and selectivities were calculated by above equations except using the partial pressure of gases instead of total pressure.

3. Results and discussion

Before discussing the results, it is necessary to mention that porous membranes which were produced by phase inversion had been tested before coating. CO_2 and CH_4 gases with different flow rates (up to 500 mlit/min) were introduced to the surface of supports. Knudsen diffusion is observed in uncoated supports that could be understand that the supports had no resistant in gas permeation.