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PDMS Coated Polyethersulphone Composite Membranes for Separation of Propylene and Nitrogen Gas Mixtures

Sayed Siavash Madaeni*, Afshin Moradi, and Vahid Kazemi Membrane Research Center, Chemical Engineering Department, Razi University, Kermanshah-67149, Iran

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ABSTRACT

series of rubber-like composite membranes were prepared for separation of gases such as propylene and nitrogen. The support layer was fabricated from different concentrations of polyethersulphone (20, 22 and 24% PES) and the coating layer was prepared from different concentrations of polydimethylsiloxane (3, 5, 7 and 9% PDMS). Permeances and selectivities of the prepared membranes for propylene and nitrogen gases and their mixtures were measured under transmembrane pressure of 1-10 bar. The influence of various parameters, such as PES concentration in support layer and PDMS concentration in coating layer at different pressures, on membrane performance were evaluated. It was shown that the membrane selectivity was increased with an increment in the feed pressure. At constant pressure for similar supports the propylene permeance and membrane selectivity were enhanced by increasing PDMS of the coating layer. For membranes with equivalent PDMS content in the coating layer, the performance of membrane was increased with PES decline in support layer. The permeability ratio of propylene over nitrogen in gas mixture (real selectivity) was low compared to the permeability ratio for pure gases passing through the membrane (ideal selectivity) at comparable operating pressure for similar membranes. At 5 bar pressure real selectivity of 3.6 was obtained while the ideal selectivity was 20.2.

Key Words:

membrane; polydimethylsiloxane; polyethersulphone; gas separation; propylene; nitrogen.

(*) To whom correspondence to be addressed. E-mail: smadaeni@yahoo.com

INTRODUCTION

Polyolefins, primarily polyethylene and polypropylene, include the largest share of the polymer market. Polyolefin manufacturing is an important operation in the petrochemical industry. In typical polymerization processes, the raw polyolefin product from a polymerization reactor contains a considerable amount of un-reacted olefin monomer. To remove the monomer, the raw polymer resin is purged with nitrogen to strip out

the monomer.

Due to the high cost of the monomers, the monomer in the off gas stream represents a significant source of profit if recovered and reused. Membrane processing has proven to be a promising technology for recovery of olefins (e.g., ethylene and propylene) from the polyolefin resin purge gases. This is a strong competitor for conventional processes such as adsorption and condensation [1]. Olefin recovery

by membranes represents a major success in the recent development of membrane technologies in the petrochemical industry.

Generally sorption and diffusion are the controlling factors for gas permeation through a dense polymeric membrane. While the diffusion step favours small molecules, the sorption step favours large and condensable molecules. For permeation of olefin molecules, rubber membranes are preferred in terms of permeability and selectivity, taking advantage of the favourable solubility properties of rubber-like polymers for olefins over nitrogen.

There are very few research articles dealing with the permeation of pure gases or gaseous mixtures through ultrathin asymmetric membranes for industrial separation purposes [2]. Liu et al. [3] investigated poly(ether-b-amide) (PEBA) composite membranes for separation of propylene and nitrogen gas mixture, to recover propylene during polypropylene production. They studied the capability of composite membranes for pure gas and propylene/nitrogen mixture. For gaseous mixture, as expected, both permeability and selectivity were low compared to pure gas permeation, which is due to interactions between the permeating components.

Currently, polydimethylsiloxane (PDMS) is the primary polymer for olefin gas separations [4]. In the mid-1950s, PDMS was found to have a much higher permeability to gases compared to almost all other synthetic polymers known at that time. Nowadays PDMS is still considered to be one of the most permeable polymers. The high permeability of PDMS is attributed to its flexible siloxane linkages. The flexible polymer chain with long range segmental motions that are active even at low temperatures makes it suitable for use at low temperatures [5].

Jiang et al. [6] reported selectivities and permeances of pure nitrogen, oxygen, ethylene, ethane, propylene and propane and their mixtures through composite polydimethylsiloxane (PDMS)-polysulphone membrane at ambient temperature and different pressures. It was found that propane and propylene plasticized the PDMS coating layer significantly both as pure hydrocarbons and as a component of gas mixtures.

In another study Jiang et al. [7] investigated the permeation performances of pure and mixed nitrogen,

ethylene, ethane, propylene and propane using a PDMS coated polysulphone composite membrane in the temperature range of -20 to 40°C. It was concluded that the permeances and selectivities of a PDMS coated polysulphone composite membrane strongly depend on the temperature and feed composition at a constant pressure for most pure and mixed gases. The permeances of propylene and propane in both pure and mixed states were significantly increased with decreasing temperature and increasing concentrations in the feed.

Shi et al. [8] investigated PDMS thin film composite membranes for the separation of propylene from nitrogen, and demonstrated the feasibility of adopting such membranes to olefin gas recovery. They found that the membrane selectivity was increased with a decrease in temperature and an increase in the feed pressure. The actual permeability ratio of propylene over nitrogen in the gas mixture was lower than the permeability ratio of pure gases at the same operating conditions.

Choi et al. [9] prepared three PDMS membranes by adjusting the mixing ratio of PDMS precursors: cross-linkable siloxane oligomer with vinyl groups and siloxane oligomer with silane groups in the presence of Pt catalyst and investigated the sorption and permeation behaviour of a series of olefins (e.g., C₂H₄, C₃H₆ and C₄H₈) and nitrogen (N₂) over the pressure range of 1-20 atm and a temperature range of -20 to 50°C with the prepared PDMS membranes. They found that the selectivity over nitrogen was greatly enhanced by increasing pressure or decreasing temperature.

Liu et al. [10] studied the effect of substrate resistance on gas permeation using flat poly(ether-b-amide)/polysulphone (PEBA/PS) and polydimethyl-siloxane/polyetherimide (PDMS/PEI) hollow fibre composite membranes. They found that the thickness and morphology of substrate can influence the membrane performance.

In spite of the recent industrial success of PDMS-based membranes for olefin recovery from polyolefin resin purge gases, not much information is available in the literature regarding the permeability and selectivity of the membrane to olefins at various operating conditions (e.g., temperature, pressure and feed composition).

In this work, membranes were fabricated in order to separate propylene from nitrogen. Membranes were prepared from PES as support layer and PDMS as active layer. The effect of operating pressure on membrane permeability and selectivity for different prepared membranes (various PES concentrations in support layer and different PDMS concentrations in coating layer) was evaluated. The ideal (pure gases) and real (mixed gases) selectivities were evaluated and compared. The combination of PES and PDMS for membrane preparation has not been tackled in the field of separation of propylene/nitrogen gas mixture. The effect of support structure on skin layer morphology and overall membrane performance is elucidated in the current research.

EXPERIMENTAL

Materials and Methods

Polyethersulphone (PES 58000) obtained from BASF (Germany) was employed as support layer of the membrane. Polydimethylsiloxane (PDMS) obtained from Dow Corning (Midland, MI, USA) was employed as active layer of membrane. PDMS (Sylgard 184 silicone elastomer kit) consisted of two parts: polymer base and hardener. Polymer base (specific gravity 1.05 g/cm³ at 25°C, viscosity 5000 cSt) was a viscous and colourless liquid which consisted of dimethylsiloxane, dimethylvinylterminated, dimethyl vinylated and trimethylated silica as well as tetra(trimethylsiloxy) silane. As labeled by the manufacturer, hardener (specific gravity 1.03 g/cm³ at 25°C, viscosity 110 cSt) was a non-viscous and colourless liquid consisted of several compounds such as dimethyl methylhydrogen siloxane tetramethyl tetravinyl cyclotetrasiloxane.

N-Methylpyrrolidone (NMP) was used as solvent for PES and n-hexane was employed as solvent for PDMS. The solvents were purchased from Merck, Germany. Two gas cylinders (propylene and nitrogen) were used throughout the trials.

Analysis

The composition of the mixed gases and permeate samples was determined using a Varian (CP-3700) gas chromatograph.

Membrane Preparation

For preparation of the membrane the asymmetric support layer phase inversion method was used. Firstly the traces of humidity in PES were removed using an oven at 110°C for 2 h. For making homogeneous solution, dried PES (20, 22 and 24 wt%) was dissolved in NMP. This solution was cast on a glass plate. The plate was dipped in water as non-solvent. The prepared membrane was immersed in water to remove the remaining solvent. The prepared support was coated with PDMS.

For preparing the coating solution, PDMS polymer base and hardener were mixed with the weight ratio of 10 to 1. The mixture was added to a volatile solvent (*n*-hexane) to obtain a homogeneous solution of 3, 5, 7 and 9 wt%. The support layer was fixed on a glass plate using tape to prevent the movement. Few drops of the homogeneous solution were cast on the surface of the support layer by a dropper to form a uniform coating layer. The solvent was immediately evaporated due to high volatility. The coating was dried during few days at room temperature.

Gas Permeation

For the experimental trials a setup with a cell was employed (Figure 1). The cell consisted of two round sections with a membrane surface area of 15.90 cm². The flux of the membranes was calculated by the

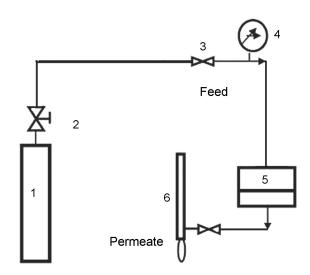


Figure 1. Schematic diagram of experimental setup for gas permeation: (1) gas cylinder, (2) pressure regulator, (3) valve, (4) pressure gauge, (5) membrane cell and (6) bubble flow meter.

permeation of propylene, nitrogen and their mixture through the system. Flux was measured on the basis of permeability as follows:

$$\frac{P}{l} = \frac{Q}{A\Delta p} \tag{1}$$

where P is permeability in cm³(STP).cm/cm².s.cmHg, l is effective layer of separation in cm, Q is gas flow in cm³(STP)/s, A is effective membrane area in cm² and ΔP is transmembrane pressure in cmHg. For all trials, firstly the flux of nitrogen was measured. This was followed by measuring the flux of propylene. This trend was due to the membrane swelling caused by passage of propylene through the membrane.

Effective separation layer is unknown and therefore P/l (called permeance in GPU = 1×10^{-6} cm³ (STP)/cm².s.cmHg) is employed. Permeance is normalized flux with pressure. Selectivity of the membranes for pure gases is defined as:

$$\alpha_{C_2H_4/N_2} = \frac{(P/l)_{C_3H_8}}{(P/l)_{N_2}} \tag{2}$$

The separation factor for mixed gas was obtained as follows:

$$\alpha_{C_2H_4/N_2} = \frac{(y_P/y_F)_{C_3H_8}}{(y_p/y_F)_{N_2}}$$

where y_P and y_F are concentrations of gases in permeate and feed.

For obtaining the error for each run and indicating the error bars in the presented graphs, at least the results for four points were collected.

RESULTS AND DISCUSSION

The experiments were performed in two steps. In the first step, the effect of applied pressure on permeability and selectivity of pure propylene and nitrogen gases passing through the membranes was evaluated, with PES (20, 22 and 24 wt%) in support layer and PDMS (3, 5, 7 and 9 wt%) in coating layer.

The membrane with superior performance in the first step was selected for extended experiments. In the second step the effect of pressure on performance of the membrane in separation of propylene/nitrogen mixture was investigated.

Pure Gas Permeation

Membranes with Different Percentages of PES in the Support Layer

Three membranes with 20, 22 and 24% of PES in the support solution and 7% of silicon rubber in the coating solution were evaluated. The effects of pressure on permeances are depicted in Figure 2. The permeability of nitrogen is essentially independent of pressure. The permeability of propylene is significantly enhanced with pressure increment. The nitrogen permeance during trials was fairly constant. Therefore the propylene permeance determines the membrane performance. The permeability of propylene was much higher compared to nitrogen. This is a typical behaviour for rubbery membranes. The observation is consistent with the physical basis of the permeation. The absorbed propylene in the membrane swells the polymer matrix resulting in enhanced solubility and diffusivity. Solubility is normally improved with increasing pressure. This phenomenon, i.e. solubility plays a vital role in the permeation of propylene [8,9].

The permeability of propylene through the 20% PES membrane was higher than the other

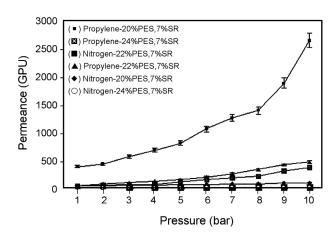


Figure 2. Permeances of membranes with different supports (20, 22 and 24 wt% PES) and similar silicon rubber.

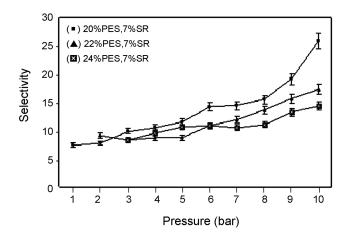


Figure 3. Selectivities of membranes with different supports (20, 22 and 24% PES) and similar silicon rubber.

membranes. The resistance of PES layer versus coating layer was negligible. This was the support layer providing acceptable mechanical strength for the membrane. However the structure of the support affects the structure of the skin layer and accordingly influences the permeability of gases. The support layer with higher percentage of PES possesses denser structure and lower porosity. High surface density of PES creates a uniform and dense skin layer [11]. The denser active layer results in less permeability for propylene. The ideal selectivities on the basis of permeabilities are presented in Figure 3. The selectivity of membrane with 20% PES in the support layer is higher than the other membranes. In other words the passage of propylene through the membrane is enhanced due to the formation of a skin layer with lower density. The permeation of nitrogen through the PDMS skin layer is negligible. Higher propylene permeability with constant nitrogen permeation results in greater selectivity.

Membranes with Different Percentages of PDMS in the Coating Layer

Four membranes with similar supports (20 wt% PES) and different coating concentrations (3, 5, 7 and 9 wt% PDMS) were prepared and compared. The membranes were coated with three layers of coating solution. Nitrogen permeance in 3% coated membrane is greater than the other coated membranes (Figure 4). This is due to formation of denser layer on the surface of membranes with higher concentrations

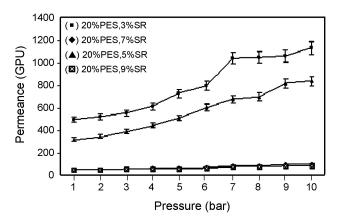


Figure 4. Nitrogen permeances through the membranes with different coating layers (3, 5, 7 and 9% SR) and similar PES.

of silicon rubber providing a resistance against the flow [11]. Propylene permeation through the membrane is higher for 9% coated membrane (Figure 5). This is due to different permeation mechanisms. Propylene intrinsically passes through PDMS readily compared to nitrogen. Higher concentration of PDMS in the membrane skin layer leads to higher permeation of propylene without pronounced passage of nitrogen. Figure 5 confirms this behaviour. The governing mechanism for permeation of organic propylene in rubber matrix is solution-diffusion. Increasing the concentration of PDMS in coating layer enhances the solubility of propylene in the coating layer. Higher propylene permeation without further enhancement in

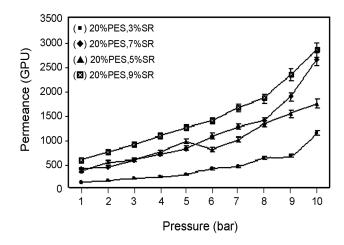


Figure 5. Propylene permeances of membranes with different coating layers (3, 5, 7 and 9% SR) and similar PES.

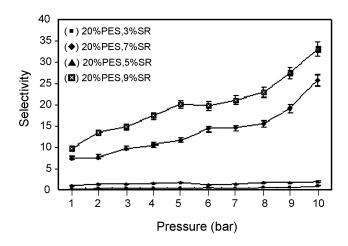


Figure 6. Selectivities of membranes with different coating layers (3, 5, 7 and 9% SR) and similar PES.

nitrogen passage results in higher selectivity for higher concentration of PDMS in the skin layer. In other words the selectivity of 9% coated membrane was high compared to the coated membranes with lower PDMS concentration (Figure 6). The obtained data indicate that the major parameter affecting the selectivity or "separation factor" is the characteristics of the skin layer. Moreover the porous sub-layer is strongly affecting the selectivity of the composite membrane.

Mixed Gas Permeation

In real gas separations, the feed is a mixture of various gases. Although the pure gas permeation data are widely used for research purposes, this is not sufficient for estimation of the real separation performance of the membrane. It is more particularly important where there are specific interactions between the gas components and the polymer matrix. The propylene permeability is significantly affected by pressure [8]. The strong pressure dependency is an indication of powerful interaction between propylene and the membrane material.

The real membrane selectivity for gas mixture was investigated in the current study. According to previous results, the membrane with 20 wt% PES in the support and 9 wt% PDMS in the coating layer was selected for gas mixture trials. Figure 7 shows the permeance of mixed gases through the membrane as a function of feed pressure for various feed concentrations. The permeance of mixed gas is

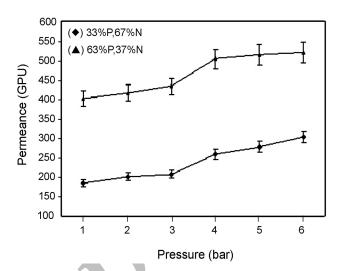


Figure 7. Permeances of different gas mixtures through the membrane (20 wt% PES and 9 wt% PDMS).

increased with increasing the feed pressure [3,8]. Higher propylene content results in higher permeance of mixed gases. This is due to higher dissolution of propylene in the membrane. The membrane is swollen by propylene enabling gases (propylene and nitrogen) to diffuse through the membrane more easily [7-9].

The real membrane selectivity for mixture of propylene and nitrogen is presented in Table 1. The ideal selectivity is added for comparison. For both, the selectivity is improved by increasing the applied pressure. However the real selectivity is much lower than the ideal selectivity, for instance 3.6 versus 20.2 at 5 bar. This is due to two factors. Firstly, the presence of olefin in the gas mixture increases the permeance of nitrogen. Secondly, the permeability of olefin in a mixture is low compared to the permeability of pure olefin due to lower partial pressure of olefin in the mixture [3,6,8].

Table 1. Membrane selectivities of mixed and pure gases.

Separation characteristics	2 bar	3 bar	5 bar
y_{p1} y_{p2} α_{mixed} α_{pure}	0.63	0.63	0.63
	0.797	0.827	0.86
	2.60	2.80	3.60
	14.5	17.9	20.2

CONCLUSION

The permeance and selectivity of the PDMS/PES composite membrane, with different coating and support layer concentrations, were elucidated for propylene/nitrogen separation. The following conclusions are drawn:

- Coating layer plays a vital role in the separation of propylene/nitrogen gas mixture. The concentration of PES in the support affects the membrane performance. The highly concentrated supports lead to a dense structure, i.e., a uniform and dense active layer. This results in less permeability for propylene.
- The membrane selectivity is improved by increasing the percentage of PDMS in the coating layer.
- The propylene/nitrogen selectivity can be enhanced by increasing the feed gas pressure.
- The real selectivity of propylene over nitrogen in the gas mixtures is much lower compared to the ideal selectivity for pure gases at the same operating pressure using similar membranes.
- The permeability of propylene is not largely affected by the presence of nitrogen. However the nitrogen permeability is significantly enhanced by the presence of propylene.

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