In the Name of God

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Preparation of Polymeric Membrane for Natural Gas Sweetening

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Dedicated
To
My Family

Abstract

In this research, the integrally asymmetric polyethersulfone membranes were prepared using phase inversion technique. The effect of operating and preparation parameters on performance of polydimethyl siloxane (PDMS) coated membranes was investigated. As an interesting result, the membrane exhibits rubbery PDMS behavior for H_2S containing feeds and displays a glassy PES membrane for CO_2/CH_4 mixed gas. The effects of sodium dodecyl sulphate (SDS), cetyle three methyl ammonium bromide (CTAB), and Triton X-100 on structure and performance of polyethersulfone membranes for carbon dioxide separation from methane were investigated. The results indicate that addition of surfactants in the casting solution increases the membrane porosity and membrane gas permeance and decreases CO_2/CH_4 ideal selectivity, except for Triton X-100 which increases CO_2/CH_4 selectivity. Asymmetric gas separation membranes of polyethersulfone (PES) and polyethersulfone/polyurethane (PU) were prepared with different blend compositions. The obtained results indicated that the presence of PU in the casting solution decreases the CO_2 permeance and enhances the CO_2/CH_4 selectivity and plasticization pressure of the PES membrane. Polyetherimide (PEI) was used as a polymeric additive for preparing an asymmetric polyethersulfone (PES) membrane. In pure gas experiments, the higher skin layer thickness and the lower porosity of the sub layer for the membrane prepared from the polymer blend with the composition of 98:2 leads to an increase in CO_2/CH_4 selectivity and a decrease in the CO_2 permeance in contrast with a pristine PES. For higher PEI contents, the gas permeance was improved and CO_2/CH_4 selectivity was decreased. We prepared a novel water insoluble Amino-Starch (AS) derivative using Williamson ether synthesis method. Introducing the AS into the PES membranes leads to a denser sub-layer and a higher CO_2 sorption capacity of the prepared membranes. A higher CO_2 permeation, lower CH_4 permeation and higher CO_2/CH_4

selectivity are the most important changes in the performance of the PES membranes caused by the incorporation of the facilitated transport in CO_2 permeation and the denser sub-layer of the prepared membranes. A novel Poly (acrylonitrile-co- N, N-Dimethylaminopropyl acrylamide) [PAN-PDMAPAM] copolymer was synthesized and employed as a CO_2 carrier in the PES membrane. An improvement can be seen in the plasticization when the PAN-PDMAPAM concentration was 0.5 and 1 wt. %. Introducing the PAN-PDMAPAM in PES membranes significantly improves the membrane performance including CO_2 permeance and CO_2/CH_4 selectivity.

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List of symbols

AN	acrylonitrile
b	Langmuir affinity (1/bar)
C	concentration of the adsorbed gas [cm^3 (STP)/cm^3 polymer]
CTAB	cetyle three methyl ammonium bromide
C_D	gas concentration on the basis of Henry's law
C_H	gas concentration on the basis of Langmuir sorption
C_H'	Langmuir sorption capacity
DMAPAm	N, N-Dimethylaminopropyl acrylamide
DMAEMA- AA	(2-N,N-dimethyl aminoethyl methacrylate)– (acrylic acid)
DMF	Dimethylformamide
DMAc	Dimethylacetamide
DMSO	Dimethyl Sulfoxide
DFT	Density Functional Theory
DSC	Differential Scanning Calorimetry
E_{AB}	energy of the complex
E_A	total energy of interacting species A
E_B	total energy of interacting species B
E_D	activation energies of diffusion
Ep	apparent activation energy of permeation [kJ/mol]
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatograph
GPU	gas permeation unit
k_D	Henry's law parameter
NMP	N-methylpyrrolidone
PES	polyethersolfune
PEEK WC	polyetheretherketone
PEG	Polyethyleneglycol
PEI	polyetherimide
PAI	poly (amide-imide)
PDMS	polydimethyl siloxane

P_0	pre-exponential factor [Barrer]
p_i	initial pressure in the module [bar]
p_f	final pressure in the module [bar]
PAAm	Polyallylamine
PAN-PDMAPAm	Poly (acrylonitrile-co-N, N-Dimethylaminopropyl acrylamide)
PEI	Polyethylenimine
PES	Polyethersulfone
PS	Polysulfone
PVSA–SA	Poly(*N*-vinyl-sodium aminobutyrate-*co*sodium acrylate)
PVA	Poly (vinyl alcohol)
PVAm	Polyvinyl amine
PU	polyurethane
$(P/l)_i$	pressure-normalized flux
R	universal gas constant [8.314×10^{-3} kJ/mol. K]
S	solubility of the penetrant
SDS	sodium dodecyl sulphate
S_D	solubility value based on Henry's law sorption
S_H	solubility value based on Langmuir-type sorption
SEM	Scanning Electron Microscopy
T	absolute feed temperature [K]
TFC	Thin Film Composite
T_g	glass transition temperatures
TGA	Thermal Gravimetric Analysis
V_m	volume of the module [cm^3]
V_p	volume the polymer sample [cm^3]
XRD	X-ray diffraction
$\alpha_{A/B}$	membrane selectivity
ΔH_S	enthalpy of sorption

Chapter one

1.1 Importance of natural gas sweetening

The worldwide attention to natural gas as a cleaner fuel and a principal feedstock for chemical industry is continuously increasing. Light hydrocarbons such as methane, as a main component, and other gases such as CO_2, H_2S, and water vapor constitute a complex mixture of natural gas. It is necessary to remove corrosive gases including CO_2 and H_2S from raw natural gas because they increase the volume of the transported gas, pipeline corrosion, and atmospheric pollution. Therefore natural gas sweetening is an important industrial gas separation process [1, 2].

1.2 Importance of membrane technology

Some of the technologies for natural gas sweetening are absorption of acid gases in basic solvents, pressure swing adsorption and membrane technology. Although the gas absorption processes are fully developed; they need the solvent regeneration and they are not suitable for small gas fields and offshore applications. Also they are not robust against change in feed composition. Similarly, pressure swing adsorption suffers from high capital cost and high energy consumption [1].

Membrane technologies are competing with other technologies because they consume less energy, they have minimum requirement of space, and they have the lowest degree of environmental pollution [1, 2]. Membrane based gas separation using different materials was investigated in several reviews [3-8]. Polymeric membranes, in contrast with inorganic membranes, have advantages such as suitable strength and processing ease [9]. Cellulose acetate (CA) has been commercialized for this purpose. Although CA membranes have

many advantages, they are limited in terms of CO_2 permeability and CO_2/CH_4 selectivity [10]. Commercial cellulose acetate membranes have a selectivity of 12–15 under normal process conditions [11].

1.3 TFC and integrally-skinned asymmetric membranes

Most common types of polymeric membrane for gas separation purposes are integrally-skinned asymmetric membrane and Thin Film Composite (TFC) membranes for their thin selective layer and consequently high performance for gas separation processes. Thin Film Composite (TFC) membrane is composed of a thin nonporous selective skin layer supported on a thick porous non-selective substrate so that the skin layer provides selectivity and the porous support provides the mechanical strength. They have a potential for minimizing the cost of membrane preparation for only a little amount of the high performance polymer is needed for the formation of the thin skin layer. The gas permeability is high because of low thickness of the dense selective layer. Finally, optimal separation performance can be obtained by management of skin and support layers independently [2, 12-14]. An integrally-skinned asymmetric membrane is made up of a very thin and dense selective layer supported on a much thicker microporous substrate. A similar material is used for preparation of these two layers at the same time and in a single process [15].

The most important problem in integrally-skinned asymmetric membrane synthesis for gas separation purposes is the formation of defects on the top of skin layer of the membrane. This challenge is overcome by using a high permeable polymeric layer on the skin layer of synthesized asymmetric membrane.

1.4 Solution- Diffusion model

The most accepted gas permeation mechanism through a polymeric membrane is the Solution-diffusion mechanism[16]. As shown in Eq. 1.1 based on the solution-diffusion model, the gas permeability is a product of diffusion D (m^2/s) and solubility S (m^3 (STP)/m^3 bar) [16].

$$P = SD \tag{1.1}$$

For an integrally asymmetric membrane, the morphology and the gas solubility of the membrane control the membrane performance and the thicker skin layer. A less porous sub-layer decreases the gas permeability and improves the membrane selectivity [17, 18].

The glassy polymers that have an intrinsic permeability of smaller than 10 Barrer possess a large solubility range, and an improvement in the solubility can effectively enhance the permeability [19]. PES has an intrinsic CO_2 permeability of 2.8 Barrer [12], so an improvement in the CO_2 solubility can improve the performance of PES membranes including the CO_2 permeability and CO_2/CH_4 selectivity.

1.5 Gas solubility in glassy polymers

Although the gas permeability of the rubbery polymers is higher than the glassy polymers, the solubility of the gases in the glassy polymers is greater than the rubbery polymers because in the rubbery polymers, gas solubility occurs just in fractional free volumes or based on Henry's law while in the glassy polymers there are microvoides or an excess free volume or Langmuir sites that adsorb the gas molecules in addition to the fractional free volume. So, the gas sorption in the glassy polymers is modeled by the dual-mode sorption model [19, 20] which can be described as follows.

$$S = C/p = S_D + S_H \tag{1.2}$$

where S is the total solubility of the gas, C is the total concentration of the gas molecule in the polymer, p is the gas pressure, S_D represents the solubility of the gas based on Henry's

law and S_H is the solubility of the gas in Langmuir sorption sites or the internal surface of the microvoids of the glassy polymer [21].

Pressure dependency of the gas sorption in the glassy polymers based on dual-mode sorption model is shown by the following equation:

$$C = C_D + C_H = k_D p + C'_H \, bp /1 + bp \quad (1.3)$$

where C_D and C_H are the gas concentrations on the basis of Henry's law and Langmuir sorption, respectively; k_D ($cm^3(STP)/cm^3$ bar^{-1}) polymer is the Henry's law solubility constant; C'_H ($cm^3(STP)/cm^3$ polymer) is the Langmuir capacity constant; and parameter b (bar^{-1}) denotes the Langmuir affinity constant [21].

The non-equilibrium excess free volume of the glassy polymers is responsible for the higher solubility of the gasses in contrast with the rubbery polymers. This means that these excess free volumes provide more adsorption sites for the adsorption of the gases in the polymeric chains. The magnitude of the non-equilibrium excess free volume of the glassy polymers is measured by determining C'_H. A higher T_g of the polymer implies an increased excess free volume of the polymer because the non-equilibrium structure of the glassy polymer results from quenching the polymer from the rubbery to the glassy state for a lower T_g and vice versa [19, 22].

The gas polarity determines the solubility in the polymers, so CO_2 is more soluble than CH_4 in the polar polymers because it has a quadrupolar moment characteristic [23]. Hence, adding a new functional group in the polymer backbone or mixing the main polymer with a more polar polymer affects the CO_2 solubility [24, 25] and CO_2 permeability and subsequently the membrane performance.

1.6 Effect of pressure on membranes performance

Pressure dependency of gas permeance is controlled by three main factors: gas solubility, membrane compaction, and membrane plasticization by high penetrating gas like CO_2 and H_2S.

Based on the dual mode sorption model; increasing the feed pressure results in a higher gas sorption and as predicted by the solution-diffusion model, higher gas sorption results in a higher gas permeance of the membrane [26].

The gas permeability of the membrane decreases by compaction processes because the free volume of the membrane reduced. In the plasticization process the chain packing of membrane disrupted and chain mobility increased and subsequently the gas permeability increases. Plasticization processes result in membrane selectivity reduction, too [27-29].

The consequent of these three factors determines the final behavior of membrane when the feed pressure increases. Glassy membranes including PES, exhibit a decrease in gas permeance and an enhancement in selectivity at the early steps of the pressure increase that means the compaction effect is the controlling factor at the early steps of the pressure increase. When the feed pressure passes a special pressure named plasticization pressure, plasticization overcomes the compaction effect, membrane behavior changes and membrane permeance increases and the CO_2/CH_4 selectivity decreases [26, 29].

1.7 Temperature dependency of gas permeability

The temperature dependency of gas permeability in a dense membrane with solution-diffusion permeation mechanism can be described by the Arrhenius equation:

$$P = P_0 \exp(-E_p/RT) \quad (1.4)$$

where P is the permeability coefficient [Barrer = 10^{-10} cm^3 (STP) .cm/cm^2.cmHg.s], P_0 is the pre-exponential factor [Barrer] and the temperature independent constant, E_p is the

apparent activation energy of the permeation [kJ/mol], R is the universal gas constant [8.314×10^{-3} kJ/mol. K] and T is the absolute feed temperature [K] [26, 30].

As can be concluded from Arrhenius equation, when $E_P>0$, an increase in the feed temperature enhances the gas permeability and vice versa.

According to the following equation, Ep is composed of two independent terms including activation energy of diffusion (E_D) and the enthalpy of sorption (ΔH_S) [43, 45].

$$E_P=E_D + \Delta H_S \quad (1.5)$$

E_D can never be a negative value and ΔH_S can be either positive or negative. Depending on the magnitudes of E_D and ΔH_S, E_P can be positive or negative.

For gas separation polymer such as air separation membranes and hydrogen removal from gas mixtures whose separation mechanism is based on size sieving, $E_D>|\Delta H_S|$; so $E_P>0$ and gas permeability increases by increasing the feed temperature [31, 32]. For glassy polymers $E_D>0$ and $|\Delta H_S| < E_D$; hence, usually $E_P>0$, which means increasing the feed temperature increases the gas permeability.

For a gas-membrane system, a higher E_p implies a larger increasing rate of the gas permeability. The size of the penetrant, membrane material and membrane structure determine the E_p [30, 33].

Larger gas species and less permeable penetrants have a higher E_p, so an increase in the feed temperature raises the permeability of larger molecules more than the smaller ones, which leads to a downfall in the membrane selectivity.

The qualitative justification of Arrhenius equation is that an increase in the feed temperature increases the diffusion coefficient of the gas molecules as well as the mobility of the polymeric chains which results in the formation of larger free volumes [34]. For rubbery polymers such as PDMS, ΔH_S may have a large negative value, so E_P can be negative [30, 31]. In rubbery polymers the relative solubility of penetrant determines its

permeability. Higher critical temperature of penetrants such as H_2S and CO_2 results in higher condensability and as a consequent higher solubility in rubbery polymers. In other words the selectivity of PDMS membrane depends on the difference in solubility coefficients of penetrants more than difference in diffusion coefficients [35].

1.8 Facilitated transport mechanism

The major problem for the use of the membrane-based CO_2 separation is the absence of membranes which have both a high permeability and a high selectivity simultaneously [36].

One of the most interesting fields in membranes processes is the facilitated transport membranes, which provides a solution for the problem of conventional membranes. In this type of membrane, a carrier reversibly reacts with carbon dioxide and increases its permeability [37, 38]. The following chemical reactions in which CO_2 rapidly and reversibly reacts with the carrier can describe the facilitated transport mechanism of CO_2 in the presence of amine groups [13]:

$$CO_2 + 2RNH_2 \longleftrightarrow RNHCOO^- + RNH_3^+$$

$$CO_2 + 2R_2NH \longleftrightarrow R_2NCOO^- + R_2NH_2^+$$

$$R_3N + H_2O + CO_2 \longleftrightarrow R_3NH^+ + HCO_3^-$$

Most of the fix facilitated transport membranes have been made as a thin film composite membrane and amine containing polymer as the separating layer has been supported on a porous membrane due to the fact that integrally skinned asymmetric membranes cannot be formed by these types of polymers because of their poor mechanical properties.