RESEARCH ARTICLE

Gas Separation by Polymer Membrane

*Santosh Walke[1], Manoj Mandake[2], Sahil Thool[2]

[1]Department of Mechanical and Industrial Engineering, Caledonian College of Engineering, Muscat, Oman.
[2]Department of Chemical Engineering, Bharati Vidyapeeth College of Engineering, Navi Mumbai, India.

ABSTRACT

Polymeric gas separation membrane has been widely used for a variety of industrial gas separation applications. This review presents the structure and property relation and describes the membrane fabrication technology. Polymers are believed to be used commercially for gas separation and hence the challenges associated with the development of membrane materials are also explained. Comparison of competitive technologies and membrane technology and some classes of polymers are also discussed in this review. The focus of the work also include Thermally Rearranged polymer (TR), Polymer of Intrinsic Micro porosity (PIMs), perfluro polymer and high performance polyimide.

Keywords: Gas separation membrane, Polymer membrane, Thermally arranged polymer, High performance polyimide, Membrane technology.

1. INTRODUCTION

The gas separation membrane market has grown significantly since its beginning in the 1970s, and continued growth is expected in the coming years as technology improves and applications expand. Previously, several review articles and monographs have chronicled overall progress in the eld as well as specific progress in applications and materials science. This review focuses on the role of polymer science in current and future materials for gas separation applications. To provide context for the materials science discussion, current applications of polymeric gas separation membranes are discussed alongwith potential future applications that may become feasible with improved membrane materials. Membrane performance is often characterized by gas throughput and separation efficiency and these properties are most commonly expressed by permeability and selectivity coefficients.

1.1. Permeability coefficient

For a pure gas permeating through a polymer film or membrane gas, permeability, PA, is dened by means of the trans-membrane pressure difference, $p2$ to $p1$, and thickness normalized steady-state gas flux, Na [1]

$$PA = Na\, l / (p2 - p1)$$

where l is the membrane thickness, $p2$ is the upstream pressure, and $p1$ is the downstream pressure.

Unlike flux, which depends upon l and delta p, PA is typically viewed, to be a first approximation being a material property that is much less dependent than ux on membrane thickness and delta p. For gas mixtures permeating through polymers, delta p is taken to be the partial pressure difference of the component of interest, and for non- ideal gases, delta p can be replaced by the fugacity difference across a membrane or lm.

Typically permeability coefficients are expressed in Barrer [2],

$$1\, Barrer = 10^{-10}(cm^3)cm\, cm^{-2}s^{-1}Hg^{-1}$$

Each polymer has a different permeability coefcient for each gas, and the faster permeation of some gases relative to others provides the basis for the use of polymers to separate gas mixtures. The range over which permeability can vary in different polymers is enormous. For example, oxygen permeability in poly acrylonitrile

(PAN), a high barrier polymer, is 2.8×10^4 Barer. At the other end of the scale, a polymer based upon an indane containing poly(diphenylacetylene) derivative has an oxygen permeability of 18,700 Bar. Diffusion coefcients are also sensitive to polymer chain flexibility and the free volume in the polymer, which depends on the amount of packing defects, gaps between polymer chains and other structural features that give rise to openings within a polymer large enough to permit penetrant diffusion.

1.2. Selectivity

A common parameter characterizing the ability of a polymer separate two gases (e.g., A and B is the ideal selectivity, A to B [3].

$$\alpha = \frac{P_A}{P_B}$$

Selectivity is also the product of diffusivity and solubility. Ideal selectivity is often treated as material property of polymer [4].

1.3. Fractional free volume

Free volume is among the most important structural variables inuencing gas transport properties in polymers. The Cohen Turnbull model predicts that diffusion coefcients increase strongly as free volume increases. This relationship is shown below, where A is a constant related to the geometric factor, molecular diameter and gas kinetic velocity, v* is a parameter related to the size of the gas molecule, g is an overlap factor introduced to prevent double counting of free volume elements, and FFV is the fractional free volume of the polymer.

$$D = \frac{Aexp(\lambda V)}{FFV}$$

In gas separation polymers, free volume is the void space between polymer chain segments that is available to assist in molecular transport. Free volume can be generated by inefficiencies in polymer chain packing in the solid state and by molecular motion of polymer chain segments, which effectively open gaps in the polymer matrix on a transient basis that allow penetrant molecules to diffuse through the polymer. Fractional free volume is calculated as the difference between the experimental specic volume (i.e., reciprocal of polymer density) and the theoretical volume occupied by polymer chain [7].

1.4. Plasticization

As the concentration of gas inside a polymer increases, the polymer can swell, which increases free volume and chain motion that, in turn, increases gas diffusion coefcients and decreases diffusion selectivity. This phenomenon is known as plasticization. Plasticization often results in higher gas ux but lower mixed gas selectivity, particularly at high pressures. One common signature of plasticization is the increase in permeability of a gas as the upstream partial pressure of that gas increases. However, strictly speaking, increase in permeability can be due to either increase in solubility, increase in diffusivity, or both, and plasticization is typically associated with increase in permeability driven by increase in gas diffusion coefcients as upstream pressure and, therefore, the concentration of gas dissolved in the polymer, increases [8]. Another common symptom of plasticization is an increase in permeability of all components in a mixture and a loss in selectivity as upstream total pressure or partial pressure of one or more components increases[9].

CO_2 is a common gas used in plasticization studies [11]. Among gases of importance in gas separation applications, CO_2 is often among the more soluble gases, and plasticization by CO_2 is widely known and studied in relation CO_2 removal from natural gas [10]. Many polymers sorb enough CO_2 at accessible pressures to strongly plasticize, so it is a convenient penetrant for such studies.

2. MEMBRANE FABRICATION AND COMPETING TECHNOLOGIES FOR GAS SEPARATION PROCESSES

2.1. Membrane fabrication

Today, all gas separation membranes are made by processes based on the concept of phase inversion because it is the only commercially viable way known for making it thin of the order of 100nm or less, defect-free membrane. To prepare membranes via phase inversion, a water-insoluble polymer is dissolved in a water miscible,

high boiling solvent or mixture of solvents; the resulting solution is often referred to as a polymer dope. This dope is then cast using a doctor blade onto a porous backing material, for at sheet, spiral wound membranes, or extruded through a hollow bre spinneret to prepare hollow bres [11]. After passing through a short air gap to allow solvent evaporation from the surface of the nascent membrane to begin formation of a thin, dense layer on the surface, the cast or extruded polymer dope is immersed in a non-solvent usually water bath. In this bath, solvent exchange and polymer coagulation produce a porous substrate with a thin, dense skin on top of it, in the case of spiral wound membranes, or on the outside of hollow bres. Often, the polymer dope concentration would be in the range of 30-35 wt%, and small amounts of a water- soluble polymer e.g., poly vinyl pyrrolidone or polyethylene oxide oligomers could be added to optimize the porous structure [6]. To reduce macro-void formation, water, alcohols or other additives are included in the original polymer dope, so that the dope is very close to the phase separation boundary before being cast or extruded [6].

2.2.   Competing technologies/membrane competiveness

Often gas separation membranes are not the dominant technology for a given gas separation application. Cryogenic distillation, pressure (vacuum) swing adsorption, and chemical absorption processes dominate commercial gas separation processes.

2.3.   Cryogenic distillation

Cryogenic distillation is no different than conventional distillation except that the temperatures are considerably lower [12]. Plate and tray distillation columns are employed at cryogenic temperatures. As in conventional distillation, temperature differences from the bottom to the top of the column allow for separation. In the case of air separation, large quantities of air are compressed, puried, cooled and then liqueed before being separated in distillation columns [13].

In addition, cryogenic separation can be used to separate hydrogen from much more readily condensable hydrocarbons. For obvious reasons, cryogenic distillation is the method of choice for the large liquid oxygen and liquid nitrogen markets as well as applications requiring high purity.

2.4.   Pressure Swing Adsorption (PSA)

It involves pressurizing a gas mixture in the presence of specic adsorbents such as zeolites, silica, alumina and activated carbon [14]. PSA can operate at ambient conditions and thus the energy costs associated with heating or cooling is minimized. These adsorbents are porous structures with extremely high internal surface areas and can adsorb one gas preferentially to the other [14]. Molecular sieves can prevent a larger diameter gas from entering the pores and can thus provide separation based on gas molecule size [15]. Once pressurization is conducted, the system is depressurized, allowing the lower absorbing gas to leave the adsorption bed rst. This depressurization step leaves the chamber enriched in the gas with the higher sorption value on the adsorbent [16]. Usually, this process involves at least two beds because one is being pressurized i.e., is being used to adsorb gases and the other is being depressurized i.e., regenerated to allow continuous operation. If operated near ambient pressure for one cycle of the process and vacuum for the other cycle, the process is referred to as Vacuum Swing Adsorption (VSA). PSA is the primary process used for hydrogen purication [16, 17]. Reneries use PSA for hydrotreating and hydrocracking processes as well as the removal of H_2S from hydrogen. PSA is also used to separate carbon dioxide from methane for natural gas purication.

2.5.   Comparison of PSA and cryogenic distillation

PSA are well suited for small scale oxygen production while cryogenic distillation is used for large scale oxygen production. PSA is the process of pressurizing and depressurizing gas to optimize gas separation. Cryogenic separation requires a combination of low temperature and high pressure to liquefy air to be separated by distillation. PSA are normally associated with capital when compared to other technology while cryogenic process require the use of numerous equipment like compressor turbine, heat exchanger, insulator and distillation column and maintenance of these equipment makes it capital intensive. A lower pressure or vacuum is used to desorb the adsorbent bed and PSA cycle can be operating close to isothermal condition without heating or cooling steps. For this reason PSA cycle is attractive to bulk separation process whereas cryogenic plant utilize cryogenic separation which requires a combination of low temperature and high pressure to liquify air to be separated by distillation. PSA is associated to low energy and cryogenic distillation is associated with high energy. PSA require low power

to operate and comparatively another require high power to operate. PSA is suitable for high and large purity while cry is suitable for medium bulk and high purity. PSA nitrogen plant needs 5 min to start up while cryogenic distillation takes 12-14hr to start up. It cannot switch off or on frequently [18, 19].

Disadvantages of PSA cycle are high gas loss resulting from the pressure release during desorption while membrane technology have compactness, light weight, low labour intensity, modular design permitting easy expansion or operation at partial capacity, low maintenance, low energy requirement and low cost for especially small sizes. While on the other side, the view membrane are expensive, certain solvent can quickly and permanently destroy the membrane. Life cycle of adsorbent is more than 10 yrs. which is comparable to that of the membrane.

2.6. Chemical absorption processes

Presently, the primary process to remove CO_2 from natural gas and power plant flue gas involves a monoethanolamine chemical absorbent-based process. When 2an-amine is reacted with carbon dioxide, a nitrogen substituted carbamic acid is formed. This is a rather unstable product which will decompose to the original amine and carbon dioxide at modest temperatures (>100 ^oC). Thus amines can be used to capture CO_2 at ambient temperatures and the amines can be regenerated and CO_2 can be collected as a gas at higher temperatures [16]. This approach provides a facile method to separate CO_2 from gas mixtures and collect CO_2 at high purity. This process is widely used and has been proposed for the collection of CO_2 for sequestration from power plant flue gas [20]. While monoethanolamine is one of the preferred amines used in this process, other similar amines such as diethanolamine, methyl diethanolamine and triethanolamine, which can also remove H_2S from natural gas streams, have been employed [16].

Drawbacks of membrane gas separation include limited ability to achieve high purity separation, lack of feasibility in large-scale operation and sometimes higher capital cost.

3. MEMBRANE PROCESS VERSES ALL OTHER TECHNOLOGIES

As noted later, membrane separation processes have favourably competed with conventional processes for a number of reasons. Membrane processes are generally more energy efcient. It offer simplicity of operation and are favourable for smaller scale operations where gas purity is not critical. It considered a "fragile" system based on 100nm dense lm thicknesses. Membranes have shown durability and reliability during long-term use even under continuous use with high pressure drop approaching 1000 psi (69 bar) in specic cases across the hollow bre or at membrane [21].

4. POLYMER MEMBRANES
4.1. Polysulphone Membrane (PS)

The Synthesis of Polysulfones can be prepared via nucleophilic aromatic polycondensation of an aromatic dihydroxy compound with a bis-(halophenyl) sulfone. It is the most chemically and thermally durable thermoplastic polymer with high rigidity (high Tg), high strength, good creep resistance, dimensional stability, and high heat deection temperature. Polysulfone remains widely used for hydrogen and air separations [22].

4.2. Cellulose Acetate (CA)

They are produced by acetylation of cellulose with a source of acetate esters, typically acetic anhydride or acetic acid, and a catalyst such as sulphuric acid.CA membranes are relatively inexpensive in part because cellulose, the raw material is an abundant and renewable resource. Applications-for the separation of CO_2 from mixtures with hydrocarbons enhanced oil recovery operations for natural gas separation [23].

4.3. PPO

It is synthesized from substituted phenols via oxidative coupling polymerization which involves the room-temperature oxidative CeO coupling of 2,6-dimethylphenol in the presence of stoichiometric amounts of oxygen.This process is catalyzed by CuCl and an amine ligand, such as pyridine. It was the rst commercialized aromatic polyether and is still being used in many industrial applications like gas separations [24]. The kinked ether linkage and the absence of polar groups suppress efcient chain packing and densication, resulting in a relatively large fractional free volume in PPO, as seen in table 1. The high free volume and the ease of rotation of the phenyl rings about the ether linkages contribute to high diffusivity and permeability [25].

Table A1.Permeability of common gases and fractional free volume

Polymer	CO_2	H_2	O_2	N_2	CH_4	FFV
Matrimid	10	18	2.1	0.32	0.28	0.17
CA	4.8	12	0.82	0.15	0.15	
PSF	5.6	14	1.4	0.25	0.25	0.14
PPO	61	61	16.8	4.1	4.3	0.18
PC	4.2		1.4	0.18	0.13	0.092
Aramid		24.5			0.1	

4.4. Aramids

Syntheses by Aromatic polyamides, or aramids, are generally produced from step polymerization or the polycondensation reaction of aromatic diamines with aromatic di-acid chlorides. The advantage is that the wholly aromatic structures of the aramid polymers give them excellent thermal and mechanical properties, which make them useful in technologies such as gas separations [26].

4.5. Polycarbonate (PC)

Synthesis-Polycarbonates are polyesters of carbonic acid (especially derived from phosgene or diphenyl carbonate) which enhances the chain packing contributes to increase O_2/N_2 selectivity in the polymer, making it more attractive for use as an air separation membrane [27].

4.6. Polyimides Matrimid (PIM)

Its synthesis by Aromatic polyimides is typically by means of the polycondensation products of aromatic dianhydride and aromatic diamine monomers. In a classic method of polyimide synthesis, a tetracarboxylic acid di-anhydride is added to a solution of diamine in a polar aprotic solvent at relatively low temperatures (15-75 ^{o}C). The advantage is that, it has high gas permeability and high intrinsic selectivity combined with desirable physical properties. It's used for gas separation. It has the best CO_2 permeability, CO_2/CH_4 selectivity and high pure gas permeability than polysulphone and polycarbonate. The main disadvantage is plasticization [28].

5. EXPECTED OUTCOME
5.1. Matrimid

Matrimid is more expensive than many other commercial polymers. It may plasticide when exposed to gas stream with condensable components like CO_2. Plasticization results due to CO_2 and CH_4 permeability increases and significant loss in CO_2/CH_4 selectivity decreases. So it needs high performance polymer that maintains separation characteristics in the presence of plasticization. So the innovative idea is the need to modify matrimid membrane via thermal treatment annealing or chemical cross linking to suppress plasticization [29].

5.2. PIM-(Intrinsic micro porosity in polymers)

It is a continuous network of interconnected intermolecular voids which forms a direct consequence on the shape and rigidity of the component macromolecules. PIM which in the solid state behave like molecular sieves. As pervaporation membranes, they show selectivity for organics over water. As gas separation membranes, they exhibit a remarkable combination of high permeability and good selectivity for gas pairs such as O_2/N_2 [30, 31].

5.3. TR polymer

It is the thermal rearrangement of ortho functional aromatic polyimide

- It increases free volume element and make size distribution uniform.
- It increases solubility and diffusivity and diffusivity provide increase in gas permeability.

There are 3 major benefits of TR membrane

1. High combination of permeability and selectivity i.e. High CO_2 permeability and good CO_2/CH_4 permselectivity .
2. Resistance to plasticization (i.e. excellent resistance to CO_2 induced plasticization) .
3. High chemical resistance [32].

5.4. Perfluoro membrane

When blending PF with TR it is observed that

a. Increase N_2/CH_4 gas separation performance.
b. Improve heating quality in natural gas [33].

The comparison of selectivity of different membranes is given in table 2.

Table A2.Comparison of Selectivity of various polymer membranes

Polymer	H_2/CH_4	H_2/N_2	CO_2/CH_4	CO_2/N_2	CO_2/H_2	O_2/N_2	N_2/CH_2
Matrimid	64	56	36	31	0.56	6.6	1.1
CA	80	80	32	32	0.4	5.5	1
PSF	56	56	22.4	22.4	0.4	5.6	1
PPO	14	15	14	15	1	4.1	0.95
PC			32	23		7.8	1.4
Aramid	245	24.5					

6. CONCLUSION

There are expanded viability of current commercial membrane material such as PPO, Aramid, Polyamide, PC, CA which have gas transport properties below new developing membrane with some plasticization.

- So we need to improve permeability and selectivity and offer resistance to plasticization that is TR and PIM.
- Within this polymer TR and PIM show best permeability and selectivity.
- Perfluoropolymer performance can improve by modifying and blending TR.

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