Chapter 6

Polymeric Membranes for O₂/N₂ Separation

Ragib Shakil^{1#}, Yeasin Arafat Tarek^{1#}, Mahamudul Hasan Rumon^{1#}, Chanchal Kumar Roy¹, Al-Nakib Chowdhury^{1*}, Rasel Das^{2,3*}

¹Department of Chemistry, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

²Department of Biochemistry and Biotechnology, University of Science and Technology Chittagong, Foy's lake, Chittagong-4202, Bangladesh

³Department of Chemistry, Stony Brook University, Stony Brook, NY 11794, USA

[#]These authors are equally contributed

* nakib@chem.buet.ac.bd, raseldas@daad-alumni.de

Abstract

Over the last few decades, polymeric membranes-based O₂/N₂ separation techniques have been progressed from a laboratory curiosity to a commercial reality. These membranes show various advantages *i.e.*, low energy consumption and cost, compared to the other conventional methods for O₂ and N₂ separation. These benefits generate a great deal of interest in industry and academia to accelerate the commercial feasibility of polymeric membranes for O₂/N₂ separation. For this, various materials have been developed in order to enhance both O₂ permeability and O₂/N₂ selectivity of the polymeric membranes. In this chapter, the recent development of various polymeric membranes, including a different polymer matrix and polymer inorganic composite for O₂/N₂ separation, is discussed.

Keywords

Membrane Technology, Polymeric Membrane, O₂/N₂ Separation, Gas Separation, Selectivity and Permeability

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1. Introduction

In the modern industrialization era, the demand for high-quality oxygen (O₂) and nitrogen (N₂) in many industrial and medical applications is constantly uprising. The technological advancement for the separation of O₂/N₂ thus plays an essential part. Many methods are still under development for highly efficient technology bring-up and reducing the production cost for O₂/N₂ purification. Membrane-based technology has shown a significant impact on gas separation over the traditional approaches *i.e.*, cryogenic distillation, solvent absorption, and solid adsorption owing to their relatively lower cost, chemical, and energy consumption, and compact design [1, 2]. Except for O₂/N₂ gas pair, the efficacy of membrane technologies has also been shown for several other gas pairs [3]. Among the membrane materials, carbon-, inorganic-, polymer-, polymer-inorganic composite-based are noteworthy [4].

However, membrane-based gas transportation is nothing new, researchers are trying to develop this process for hundreds of years [5]. Usually, there are two types of membrane available such as porous membrane and non-porous or tight membrane. Porous membrane separation includes Knudsen-diffusion, and molecular sieving, whereas the non-porous membrane follows solution diffusion mechanism [6]. In between Knudsen-diffusion and molecular sieving, the pore size allowed for Knudsen flow is relatively higher which limits the separation factor of Knudsen-diffusion [7]. But the molecular sieving shows more efficacies in gas separation due to its smaller pore size, which only allows passing the smaller molecule. Alternatively, diffusion is the only mode of transport in the solution-diffusion model. The gas molecules to be transported must be dissolved in the membrane first. The solution-diffusion model takes the general approach of assuming that the chemical potentials of the O_2/N_2 and permeate fluids are in equilibrium with the neighboring membrane surfaces, allowing sufficient chemical potential expressions. The mechanisms of porous and non-porous membrane technology for gas separation are shown in Fig. 1.

Figure 1. Different mechanisms of porous and non-porous membrane technology for gas separation.

Polymer-based membrane materials have drawn great attention because of their lightweight, low cost, and easy fabrication process [8–10]. Rather, the efficacy of polymeric membranes is quite high because it usually follows the solution-diffusion mechanism for gas separation which is controlled by the permeability and selectivity. The gas permeability can be calculated by using Eq. 1. According to the mass transfer mechanism, the diffusion coefficient depends indispensably on the size of the feed gasses (N_2 , O_2 , CO_2 , CH_4 , etc.) where a gas with a smaller molecular size has a higher diffusion

coefficient [11]. This confirms the purity and selectivity of the polymeric membranes. The conventional polymer membranes are rigid, fragile, and glassy, which attribute free volume in the polymeric matrix [12]. Whereas, the flexible rubbery polymeric membranes have a higher free volume which depicts a higher diffusion coefficient [13]. The solubility is the ratio shown in Eq. 2 of polymer concentration and adjacent polymeric gas pressure.

$$P_g = S \times D \quad (1)$$

$$S = \frac{c}{p} \quad (2)$$

where P_g is gas permeability, S is gas solubility, D is the effective diffusion coefficient, c is the concentration of gas in polymer, and p is the pressure of the gas.

However, at low temperatures and pressure, the polymeric membranes should achieve limited permeability and selectivity, which makes these membranes limited in applications. To overcome the permeability and selectivity issues, polymer surface modification including functionalization and mixed polymer matrix are being adopted nowadays [14–17]. The surface functionalization of a polymer membrane improves the surface properties. Whereas, a combination of an inorganic, carbonaceous, metal-organic framework (MOF), etc. with polymer membranes generates a new type of polymeric membrane termed as mixed polymer matrix membrane (MPMM). When the pore diameters of the additive materials *i.e.*; MOFs/zeolites are higher than the size of one gas molecule but smaller than others, the permeability will be improved during the separation process [18, 19]. This leads to an economical advancement in large-scale separation for medical and industrial applications. This MPMM was firstly introduced in the early '80s and still booming to the next generation gas separation membrane technology [20].

The motivation of the chapter is to provide an overview based on various requirements of the polymeric membrane's technology being used through the present day to enhance the selectivity of O₂/N₂ separation. Different types of physical and chemical modifications of membranes for better performance are discussed. An attempt to describe the current strategies in the developments of various polymeric membranes and their suitability for O₂/N₂ enrichment are also considered and well corroborated in this chapter.

2. Types of polymeric membranes

Generally, polyamide (PA), polydimethylsiloxane (PDMS), polyaniline (PANI), polysulfone (PSf), polyimide (PI), polyurethane (PU), polypropylene (PP) etc. are the basic components of the polymeric membranes used in O₂/N₂ gas separation. Among them, PSf shows its superiority over others because of its higher selectivity and permeability with significant mechanical properties. But the PSf possess moderate chemical and thermal stabilities [21]. To overcome this, nowadays polyimide has become popular for its excellent thermal and chemical stability with generous mechanical properties [22]. Polyurethane-based membranes have microstructure but its hard segments of urea or urethane in polymer network limit the applications in gas separation [23]. Efforts are continuously putting on the improvement of overcoming those limitations and enhancing the gas separation efficiency. In addition, detailed discussion on various polymer compositions and their membrane fabrication techniques can be found in the following sections.

2.1 Asymmetric membranes

Asymmetric membranes are composed of a dense and thin top-layer supported by a porous substrate-layer in the same polymer matrix as shown in Fig. 2. The thin layer termed as skin layer or active layer that directly affects the separation process, whereas the thicker porous membrane called as sub-layer or bottom layer that ensures mechanical support to the top layer. The top layer fabrication processes and their optimization play a governing role in the gas separation and may influence the gas permeability and overall selectivity. However, to confirm the significant permeability, the top layer must be very thin, because gas permeability has an inversely proportional relation with the layer thickness for asymmetric membrane [25]. Based on the thickness, the top layer is two types *i.e.*; ultrathin and hyperthin. The ultrathin layer will have a thickness of 1000–5000 Å, where the thickness of the hyperthin layer is less than 1000 Å [26]. Moreover, it should be confirmed that no defects are existing in the top layer because even a tiny defect could be a sensitive issue for the gas separation [24]. Contamination may occur at the permeate gas, which is unwanted, can pass through a separation membrane having defects in the thin layer. The defect-free layers follow the solution diffusion mechanism, whereas the defective layer's transport gas via the Knudsen mechanism during gas separation as discussed in the introduction [24]. However, the bottom layer attributes no significant effects on the gas separation but the structural design e.g. having large pore size to minimize excess mass transfer resistance [27].

Figure 2. Gas separation mechanism in a typical asymmetric membrane.

Interfacial polymerization is commonly used for preparing an asymmetric membrane [28]. The morphology of the membrane is directed by the solidification and the phase separation of the polymer solution [29]. Usually, the phase separation is conducted by dry-wet phase, wet phase, or dry phase processes [30]. Nonetheless, there are several factors including the rheological properties, solvent ratio, the concentration of polymer solution, and the solidification time, etc. affect the gas separation performance [29]. Table 1 summarizes some recent progress in the asymmetric membrane for O₂/N₂ separation.

Table 1. Asymmetric polymeric membrane for O₂/N₂ separation

Membrane Compositions	O ₂ /N ₂ Selectivity	O ₂ Permeability GPU	Top layer thickness (Å)	References
PI	6.3	65	-	[31]
^a PC	5.3	36	-	[31]
PI	6.6	12	730	[32]
^b PES	5.8	9.3	470	[33]
PSf	7.3	6.9	-	[34]
PES	6.2	12	-	[35]
PES	5.7	15.8	-	[35]
PES	6.8	14.3	600	[36]
^c PLA	1	0.3	-	[37]
PSf	4.5	3.4	-	[38]

^aPolycarbonate (PC), ^bPolyethersulfone (PES), and ^cpoly (lactic acid) (PLA).

2.2 Copolymer and blended polymeric membrane

There is a certain difference between copolymer and blended polymeric membrane. The copolymer membrane is the result of the co-existence of multiple monomers [39]. On the contrary, polymer blend membranes contain homopolymers, which generally appear after the synthesis [40]. The copolymerization including (a) homopolymer, (b) alternating copolymer, (c) random copolymer, (d) block copolymer, (e) graft copolymer, etc. Of them, block copolymers have shown excellent structural formation for better gas separation [41]. The resulting membrane yields high free volume sites, high thermal decomposition temperature, high glass transition temperature, and high selectivity towards the O_2/N_2 separation [41]. However, some very common examples of block copolymer-based membranes are as follows: tetra-methyl-hexafluoro-naphthalene polysulfone (TMHF-NPSF), hexafluoro-naphthalene polysulfone (HF-NPSF), tetramethyl- naphthalene polysulfone (TM-NPSF), etc. as shown in Fig. 3. Among those block copolymers-based membranes that follow the O_2/N_2 gas separation permeability order: TM-NPSF < HF-NPSF < TMHF-NPSF [24]. This order is closely related to the size of the free volume membranes cavity. As the size of the groups present in the NPSF moiety increased, the cavity size also improved. As a result, increasing of gas flux is expected with the available free space in the moiety [12]. Moreover, this cavity size could affect the selectivity and the permeability of the membrane performance in the O_2/N_2 gas separation. However, the cavity size is inversely related to selectivity and directly proportional with gas permeability [42]. Some exceptions are also observed. Such as in the case of TMHF-NPSF membrane, high permeability with high selectivity of O_2/N_2 separation [42].

Figure 3. Effect of side groups on the selectivity and permeability of O_2/N_2 separation. (a) Structures of TM-NPSF, HF-NPSF, and TMHF-NPSF. (b) Relation of O_2 permeability with O_2/N_2 selectivity.

Polymer blending is a membrane fabrication technique where multiple polymers are combined together. As a result, different physical properties arise in the fabricated polymer blend membrane from different constituents. One of the major concerns during the fabrication process is the miscibility of different polymers which have direct effects on gas selectivity and permeability as revealed in Table 2. The homogeneity attributes to the quality of the fabricated polymer membrane. For example, PLA homopolymers blended from L96D4:L88D12 with the ratio of 8:2 show much better O₂/N₂ selectivity than alone L96D4 homopolymers [43]. The higher crystallinity of (L96D4) homopolymer in the PLA (L96D4:L88D12) polymer blend is the reason behind the enhanced permeability. It is mentionable that the permeability is proportional to the crystalline structure of the homopolymers [44].

Table 2. Composition of polymer blends in O₂/N₂ separation.

Membrane Compositions	O ₂ /N ₂ Selectivity	O ₂ Permeability (barrer)	References
^a SBR	5.8	602	[45]
^b SBR/NR	2.9	1457	[45]
PLA (L ₉₆ D ₄ /L ₈₈ D ₁₂)	6.2	0.34	[43]
^c PVP/ ^d EC	5.9	3.10	[46]
^e 6FDA-TAB	5.9	15.2	[47]
6FDA/PMDA-TAB	12.5	0.453	[47]

^aStyrene-Butadiene Rubber (SBR), ^bNatural Rubber (NR), ^cPoly(4-Vinyl-Pyridine) (PVP), ^dEthylcellulose (EC), and ^e4,4'-Hexafluoroisopropylidene Diphthalic Anhydride-1,2,4,5-Tetraaminobenzene (6FDA-TAB).

2.3 Polymer of intrinsic microporosity

To further the advancement of polymeric membranes, researchers introduce a new type of polymer called polymer of intrinsic microporosity (PIM) [48]. The amorphous PIM, as shown in Fig. 4, has special twisted or bending features with porous and rigid polymeric network that provides high surface area and large free volume. As a result, it shows high O₂ permeability and O₂/N₂ selectivity. For example, PIM ladder polymers have introduced two side groups of trifluoromethyl and phenylsulfone which provide high selectivity for O₂/N₂, as well as the O₂ permeability, remain high due to the extensive surface area/free volume [49].

Figure 4. Structure of an amorphous and intrinsic microporous polymers.

Besides this, another type of microporous polymer can be fabricated by thermal rearrangement (TR), and it is termed as TR polymers [50]. During this fabrication process, a lot of cavities are found which are responsible for the microporous structure of the polymer matrix. The rigid microporous structure possesses improved surface area with high free cavity volume [51]. Nevertheless, the hardness control of the TR polymer is still a challenge to the researcher. During the thermal conversion at high temperature, the structure of these TR polymers become brittle [52]. Researchers are still trying to fabricate some higher degree of TR polymers with high tensile and elongation strength to enhance the gas separation performance. In Table 3 some of the PIM and TR-based microporous polymers are listed out.

Table 3. O₂/N₂ selectivity and O₂ permeability in PIM and TR-based microporous polymeric membrane.

Membrane Compositions	O ₂ /N ₂ Selectivity	O ₂ Permeability (barrer)	Ref.
PIM-1	4	370	[53]
PIM-7	4.6	190	[53]
PIM-1	3.3	1610	[53]
PIM-1	3.3	785	[54]
PIM-1	3.2	1133	[55]
^a TFMPSPIM 1	4.6	156	[55]
TFMPSPIM 2	4.1	307	[55]
TFMPSPIM 3	3.5	560	[55]
TFMPSPIM 4	3.3	736	[55]
PIM-PI-1	3.1	151	[56]
PIM-PI-3	3.6	85	[56]
PIM-PI-8	3.4	545	[56]
^b TR-DAR-350	7.1	5.1	[57]
TR-DAR-350	538	4.1	[57]

^aTrifluoromethyl phenylsulfonyl polymer intrinsic membrane (TFMPSPIM), ^bThermal rearrangement-diaminoresorcinol (TR-DAR)

3. Drawbacks of conventional polymeric membranes

Fabricating a polymeric membrane with high permeability and selectivity is the most demanded topic in O₂/N₂ gas separation. Most of the conventional polymeric membranes show a trade-off between permeability and selectivity, (describe in section 2.2). This can be depicted in the Robenson trade-off diagram [58]. According to this trade-off, most of the conventional polymeric membranes occupy around the prior upper bound. This may result from the lower surface area, less free volume size, uncontrolled morphology, etc. However, to overcome these challenges, new approaches like surface modification of polymer surface or mixing of inorganic/other materials with a polymer to produce mixed polymeric membrane have been adopted.

4. Surface modification of polymeric membrane

Modification of polymeric membrane surface has taken great attention to improve the polymer/membrane surface properties which could enhance O₂/N₂ selectivity and O₂ permeability. Chemical modification of polymeric membrane results in a compact and tight polymeric structure, thus enhance the selectivity and permeability [59, 60].

Crosslinking modification and layer coating are the most common modification processes for polymeric membranes for O₂/N₂ separation.

4.1 Crosslinking modification

Generally, cross-linking results in compact packing density and can hinder the mobility of polymer chains [61]. It often enhances the membrane performance and stability in O₂/N₂ separation process. There are several techniques introduced for cross-linking modification *i.e.*, thermal modification, chemical modification, ion beam irradiation, plasma treatment, and UV irradiation [44-47]. In the UV irradiation technique, the O₂/N₂ selectivity increases but there is a certain decrease in O₂ permeability [62, 63]. As the mobility of polymer chains is restricted in the polymer matrix that decreases in the gas permeability. To overcome these issues, a new technique is introduced where reactive oxygen is combined with UV radiation [64-66]. This process is termed as UV-ozone treatment shown in Fig. 5. However, long exposure to UV may cause a decrease in both O₂/N₂ selectivity and O₂ permeability [67].

Usually, chemical modification involves wet or chemical reactions, often used to modify the polymer membrane structure for better O₂/N₂ gas separation [65]. A general approach for chemical modification is dipping or soaking the polymeric membrane into a reagent solution [14]. The soaking/dipping time is very important to control the degree of cross-linking [65]. Generally, the chemical modification includes oxidation, grafting, etching, plasma polymerization, etc.

Heat treatment is another approach in which the polymeric membrane is condensed/compressed/shrunk resulting in a higher packing density of the polymer chains. Due to this higher packing density, substance resistance increases. Thus, the permeability of the large molecule *i.e.* N₂ decreases and the O₂/N₂ selectivity of the membrane increases after this treatment [68]. The heat applied in this process plays a vital role where a higher temperature results in a decrease in both selectivity and permeability. This method is often utilized as a post-treatment procedure for O₂/N₂ separation.

To date, the ion beam techniques have shown their extensive applicability for the modification of the membrane surface to enhance the O₂/N₂ gas separation performance. As ion beam irradiation-induced the polymer chain functionalization, various properties of the membrane can be tailored by adopting this technique [69]. The increase in free volume and the rigidity due to the cross-linking of the polymer chains attribute a high O₂/N₂ selectivity and O₂ permeability of the polymeric membrane. However, a non-selective resistance layer is formed when high irradiation is applied and decreases both in selectivity and permeability [70]. Generally, ion beam techniques include ion irradiation,

ion implantation, and focus ion beam where the ion irradiation and the ion implantation involve *ex-situ* and alternatively, the focus ion beam involve *in-situ* modification [71]. They are all pure physical processes as none of them introduces any foreign species into the targeted polymeric membrane. In addition, a great advantage of ion beam techniques over other techniques is their controllability and repeatability.

Figure 5. A visualization of UV-Ozone treatment on the surface modification of the polymeric membrane.

The plasma treatment gives the most satisfactory techniques compared to the other polymer modification techniques. The advantages are the multilayer film formation, controlled surface modification, eco-friendly, deposition of highly cross-linked polymer, etc. The fundamental objective of plasma treatment is to modify the surface with specific functional groups like (—NH_2 , —OH , —CHO , —COOH) groups are introduced for pharmaceutical and medical purposes [72].

Figure 6. Surface modification of polymeric membrane by plasma treatment and plasma polymerization mechanism.

These surface groups attribute higher gas selectivity. Generally, for O_2/N_2 separation, various types of gas like N_2 -containing gases, fluorine/chlorine-containing gases, inert gases, etc. are used in plasma treatment for generating free radicals under plasma conditions to initiate the modification process [73]. The free radicals are produced from the inelastic collision between the electron in the plasma and the polymer surface [74]. The free radicals play a crucial factor as the degree of modification highly depends on the density of the free radicals. For a complete modification, a high density of free radical is required where a low density free radical results in incomplete modification. In between them the NH_3 and N_2 plasma treatment enhance both the O_2/N_2 selectivity and O_2 permeability [74]. Whereas, the fluorine-containing gases/fluorination and the chlorine-containing gases/chlorination may result in an increase in selectivity but a decrease in permeability [75]. The higher selectivity attributes from the renovation of the physical structure of the polymeric membrane and the low permeability results from the decrease in segmental mobility and cross-linking formation of the polymer chain. Modification with other plasma-like ethylenediamine plasma can also attribute a higher selectivity and permeability [24]. The treatment time and plasma power play important roles in plasma technique. Longer treatment time does not have any effect on the gas selectivity, meanwhile, a high-power plasma accompanies microcracking in the surface layer which results in a decrease in selectivity [76]. A schematic illustration of plasma polymerization mechanism and plasma-induced modification of polymer membrane is shown in Fig. 6.

4.2 Coating

Surface coating is an advanced technology for the modification of the membrane that is used vastly in large-scale industrial applications. In this technique, the membrane surface is coated with another layer which even has the possibility to be penetrated into the pores of the membrane. Though this technique suppresses the cost and power utility, the major challenge is to modify the polymeric surface with a stable coating layer [77]. This is due to the weak interaction between the coated layer and the surface of the membrane. Some common methods like cross-linking and sulfonation are introduced to address the coating layer on the polymeric surface. The coating is generally carried out via solution coating and plasma polymerization.

The layer-by-layer technique has shown to be a successful approach in membrane surface modification for O₂/N₂ gas separation process. As an example, PANI has great O₂ selectivity owing to its dense polymeric structure and electrical conductivity [78]. On the other hand, pure PANI films have weak mechanical characteristics, and thus PANI membranes have lower permeability. When PANI is coated with another polymeric membrane-like porous polyvinylidene difluoride, both the mechanical properties and permeability are enhanced [79].

On the other hand, plasma polymerization coating that is also termed as vapor deposition coating provides ultrathin layers with largescale pinhole. In presence of a plasma discharge exposure, organic gas molecules undergo repeated fragmentation and provide molecular radicals. As a result, polymerization occurred via the combination of these radical molecules in the very next stage [80]. The discharge power and monomer flow rate are the major issues in controlling the morphology and the deposition rate. However, as discussed in section 4.1, the presence of halide shows better performance in the O₂/N₂ separation. For example, if fluorine present in the solvent, the efficiency of oxygen sorption improved. Fluorine content might be enhanced, if the percentage of hexafluorothene increased in the mixed gases. This leads to high performance in O₂/N₂ gas separation via improving both selectivity and permeability. Some O₂/N₂ selectivity and permeability of thin plasma polymeric membranes are listed in Table 4.

Table 4. Thin plasma polymers-based membranes for O₂/N₂ separation.

Membrane Compositions	Ratio of monomer gas mixtures	O ₂ /N ₂ Selectivity	O ₂ Permeability (barrer)	Ref.
PSf	-	5.1	4.5	[81]
MP Milipore VSWP 4700	CH ₄ / ^a HFP (1:3 mole ratio)	2.8	65	[82]
PSf	^b 4-Vpy	4.7	1.3	[81]
Aluminium oxide and sinter glass	H ₂ /C ₂ F ₆ (1:1: volume ratio)	3.4	20	[83]
NR	4-Vpy	5.8	135	[81]

^aHexafluoropropene (HFP), ^bVinylpyridine (Vpy).

5. Mixed polymer membrane

Mixed matrix membrane (MMM) is a scalable membrane technology to make it more applicable by dealing with the conventional polymeric membrane drawbacks. MMM is a heterogeneous polymer composite in which a polymer matrix contains some other filler materials. The combination of the polymer matrix and the filler materials provide significant improvements, especially for the glassy polymer. Especially, the particle surface has poor adhesion interaction including hydrogen bonds, and London forces, etc. within the polymer network. That might have improved its cavity-free surface area through the formation of voids around the filler materials. As a result, high permeability is expected, but selectivity reduces. To overcome this, the researchers introduce several surface modification techniques including surface functionalization methods, and modification in fabrication technique, etc. In the surface functionalization process, various coupling agents are used to improve the binding side among the inorganic fillers and the polymer network [64, 65]. Long-chain alkyl amine is a very well-known coupling agent. It is reported that when filler particles are functionalized with this coupling agent, the polymer membrane enhances significant permeability by controlling higher selectivity [84].

It is also possible to enhance the significant separation performance by small changes in the fabrication process, either using priming or annealing techniques [66, 67]. In the priming process, the inorganic filler is firstly being enveloped with a tiny amount of polymeric solution. In the very next step, the rest of the polymers are dispersed in the solution. This two steps process provides a defect-free MMM by improving the filler and polymer network interactions [24]. Zeolite is able to get focus on MMM membrane fabrications for their suitable size and cavity shapes. These help to reduce the gas sieving discrimination. Among other zeolites, zeolite 4A (pore size of 3.8 Å) is more suitable for

the O₂/N₂ separation through the precise selectivity of the O₂ and N₂ gas depending on the size and shape. Though alone zeolite is able to improve the selectivity but permeability suffers in the O₂/N₂ separation. To overcome this, sometimes zeolite is used as a filler material with functionalized polymer matrix [85, 86], and hence the O₂/N₂ permeability with maintaining the selectivity can be achieved.

On the other hand, MOF shows even better O₂/N₂ separation in comparison with zeolite and other fillers. In a typical MOF structure, organic moiety connected with metals or metal oxides generates microporous cavities with multiple dimensions [19, 88]. When MOF present in the MMM, the structural improvement provides sufficient surface area to the membrane for O₂/N₂ gas separation. For example, in presence of MOF in the MMM matrix, enhanced significant O₂/N₂ separation performance [89]. Particularly, ZIF-8 and PSf composite membrane exhibits large O₂ permeability and O₂/N₂ selectivity compare to pure PSf alone. The tiny cavity of ZIF-8 helps to enhance the resulting O₂/N₂ separation with improved the ZIF-8-PSf membrane performance with increasing adverse effect including the total defective surface area in membrane surface. In Table 5, the O₂/N₂ selectivity and permeability of some mixed polymers are listed out.

Table 5. O₂/N₂ selectivity and permeability of some mixed polymers-based membrane

Membrane Compositions	Filler	Inorganic filler loading (wt%)	O ₂ /N ₂ Selectivity	O ₂ Permeability (barrer)	Ref.
PSf	Silicalite-1	16	4.3	2	[89]
PSf	Zeolite 4A	60	4	23.30	[86]
PSf	Silica	0.1	6.4	15.83	[90]
PSf	SWNTs	10	5.4	1.23	[84]
PSf	ZIF-8	16	8.3	2.6	[89]
^a PMMM	Zeolite 4A	20	5.01	2.04	[24]
PI (Matrimid)	^d CMS	36	7.9	3	[87]
^b PTMSP	Zeolite	5	3.03	885	[91]
^c PVAc	^e CuTPA	15	6.79	0.624	[92]

^aPoly (Methy-l-Methacrylate) (PMMA), ^bPolytrimethylsilylpropyne, (PTMSP), ^cPoly (Vinyl Acetate) (PVAc), ^dCarbon Molecular Sieve (CMS), and ^eCopper and Terephthalic Acid (CuTPA).

6. Polymer magnetic membranes

The most realistic strategy to obtain "smart" membranes is to combine polymeric membranes with inorganic magnetic nanoparticles that typically show attractive surface properties when activated with static or alternating magnetic fields of different

frequencies. The magnetic properties of O_2 and N_2 are different where O_2 is paramagnetic also having relatively high magnetic susceptibility and N_2 is diamagnetic having negative and low magnetic susceptibility. When magnetic nanoparticles are dispersed in one side or in both sides of the polymeric membrane, the O_2/N_2 shows different response in the externally applied magnetic field as the magnetic properties of O_2/N_2 are different. Because of the paramagnetic behavior and higher magnetic susceptibility of O_2 , the magnetic membrane shows higher affinity towards the O_2 molecules [93]. Thus, the O_2 molecules can pass through the magnetic membrane. This is the basic mechanism of the magnetic polymeric membrane separation process. To synthesis polymeric magnetic membrane, the membranes that can effectively change the pore size in the ultrafiltration, either by static magnetic fields or by high-frequency magnetic fields and thermo-responsive hydrogels are used [94]. The polymer magnetic membrane can be synthesized in two ways: (i) dispersing the magnetic nanoparticles (as magnetic filler nanomaterial) in the polymeric matrix, and (ii) magnetic nanoparticle coating on the polymeric membrane (surface modification) [95-98]. The preparation method highly affects the membrane morphology, thus O_2/N_2 separation performance of the polymeric membrane. Compared with magnetic nanoparticle dispersion on the polymeric membrane, the magnetic nanoparticle coating or surface modification shows higher O_2 permeability as well as the O_2 mass transfer coefficient. Generally, ethyl cellulose (EC), linear polyimide (LPI), hyperbranched polyimide (HBPI) and poly 2,6-dimethyl-1,4-phenylene oxide, and magnetic nanoparticles like ferroferric oxide (Fe_2O_3 and Fe_3O_4) or a permanent magnet like neodymium, praseodymium, ferrite, etc. are used to fabricate a smart polymer magnetic membrane [70–73]. The permeability of O_2 highly depends on the magnetic field induction. The O_2 permeability increases with the increase in the magnetic field. HBPI polymer-based membrane shows better magnetic field induction and thus, better O_2 permeability than that from LPI and EC [99, 100]. However, the O_2/N_2 separation not only depends on the external magnetic field but also on the loading of magnetic nanoparticles. In between the magnetic nanoparticles mentioned above, ferroferric oxide attributes higher O_2 permeability and O_2/N_2 selectivity owing to the increased magnetic field of Fe_2O_3 and Fe_3O_4 nanoparticles [24]. However, the O_2/N_2 selectivity is not that high. Hence, further research/investigation is needed to control the surface morphology. A schematic illustration of the polymeric magnetic membrane is shown in Fig. 7.

Figure 7. Illustration of the polymeric magnetic membrane.

7. Factors affecting O₂/N₂ separation

Like any other fabrication process in polymer science, there are some crucial operating conditions exist whose control the O₂/N₂ separation performance. First of all, the gas feeding pressure, secondly the temperature issue, thirdly the composition of gases, and lastly feed flow rate through membrane all of which affect the permeability and selectivity of O₂/N₂ gas during the separation process. With all the modifications related to the membrane described above in sections 4 and 5, the proper optimization of those conditions is also a must.

7.1 Pressure

The actual influence of pressure on the O₂/N₂ gas separation varies from membrane to membrane. Based on the composition of the membrane, the driving force of O₂/N₂ gas is controlled by the pressure at the feed side, atmospheric pressure applied for permeate gas, and the vacuum nature of the permeate gas [101]. Usually, it has been seen that the increase in the feed gas pressure with the decreased permeate pressure, the productivity and recovery enhanced. But this often leads to decrease the membrane surface area may be due to collapsing of some pores. Some studies have shown that the separation factors of O₂/N₂ eventually decrease upon increasing feed pressure [102]. Alternatively, some study shows that the feed pressure can control the permeability to a certain point. Above that certain point, the increase in the feed pressure will decrease the permeability of O₂/N₂ gas in the membrane [103]. A more interesting issue has also been reported that the O₂/N₂ permeability is completely independent of feed gas pressure as well as the selectivity of the O₂/N₂ is also constant [104]. So, the above-stated conditions regarding pressure are valid for different sorts of polymeric membranes.

7.2 Temperature

The temperature has a definite effect on the O₂/N₂ selectivity and permeability. For a nonporous polymer membrane, the gas permeability (P_g) is related to the solubility and diffusivity coefficient as shown in preceding Eq. 1. Again, this solubility and diffusivity are the functions of temperature. As a result, the permeability is prominent and selectivity is controlled by the temperature during the gas separation process. The permeability of O₂ usually enhances upon the raise of the temperature which is ultimately good for the O₂/N₂ separation process [105]. Nevertheless, increasing the temperature may hinder selectivity. It is due to high temperature often causes a lower O₂/N₂ solubility ratio, which results in lower diffusivity and ultimately lower selectivity [106]. The lower selectivity is always unwanted for efficient gas separation. For a high-quality O₂/N₂ separation, a higher degree of selectivity is always required. All of these evidences clear that the operative temperature should be optimized for balancing both the permeability and selectivity for a better-quality gas separation.

7.3 Feed flow rate and flow configuration

Most of the commercially available membranes for O₂/N₂ gas separation are composed of asymmetric hollow fibers. The hollow fibers have two different sides *viz*; bore side and inner side for flowing O₂/N₂ gas molecules during the separation process. Usually, most of the feed gas molecules pass through the bore side or internal side and it results in better separation performance than the shell-side or the outer side of the fibers. The pressure of the feed gas is really important to maintain the gas separation process efficiently in long term processes. The increase in the feed gas pressure can result in the expansion of the bore but compress the shell-side of the fiber [107]. If the bore size as showed in the Fig. 8 increases, that may enhance the permeability of gases but can reduce the selectivity [108]. As well as, the compression of the shell-side can also negatively affect the overall performance of the gas separation. However, the expansion in the bore side may occur due to the stacked gas molecules, and this effect is termed as concentration polarization [109]. Concentration polarization is destructive for the longevity and the separation performance of the membrane. The solution is related to the proper optimization feed flow. Usually, at low atmospheric pressure and high feed flow rate, the enrichment of O₂ is the highest. On the contrary, for better N₂ enrichment, high atmospheric pressure and low feed flow rate are required.

Figure 8. Illustration of the hollow fiber in a polymeric membrane.

7.4 Feed composition

As feed composition directly impacts the solubility of gas molecules and their sorption-diffusion process during the O_2/N_2 gas separation, this is also considered as a vital factor to be considered. In a multiple component-based feed gas, the separation process is hindered by the coupling effects of multiple components [110]. Besides, if there are any condensable species being present in the feed gas, then the membrane could be plasticized. Therefore, the longevity issue is mostly dependent on the composition of the feed gas. In the case of only O_2/N_2 , if the feed pressure increases, the permeability of O_2 increases but reduces in the case of N_2 . Thus, the optimization of feed gas composition and other controlling parameters are simultaneously important for controlling the performance of O_2/N_2 gas separation.

Conclusion

Over the past few years, the polymeric membrane technology improved enormously for O_2/N_2 gas separation. Researchers are now trying to optimize these classical membranes' performance using various nanomaterials. In addition, fabrication of new membranes using some novel polymers is an ongoing process for gas separation. Besides synthetic polymers, we encourage to use biopolymer such as nanocellulose, chitin nanofiber etc. for such application because of their biodegradability and cost-effectivity. Overall, the efficiency of the polymeric membranes highly depends on the polymeric membrane materials, manufacturing process as well as membrane operating conditions. In order to boost up the permeability and selectivity of gas molecules, the mixed polymeric membranes, polymer magnetic membranes, cross-linked and selective layer membranes are still need to be improved. Though the fabrication of polymeric membrane with great molecular selectivity is very challenging, this technology is consequently anticipated to

be capable of competing with the existing separation techniques, to massively separate O₂/N₂ gas to meet industrial and medicinal demands.

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