Fabrication of Polymer Based Mix Matrix Membrane - A Short Review

Iqbal Ahmed¹, Zainal Abidin Mohd Yuso², M.D.H. Beg¹
¹Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia
²University Kuala Lumpur, Malaysian Institute of Chemical and Bioengineering Technology, 78000 Alor Gajah, Malacca, MALAYSIA , zainalabidinm@micet.unikl.edu.my

Abstract-- The type for novel preparation technique of membranes in tough and inconsiderate environments is the improvement of new tough, high performance materials. The modular nature of membrane operations is essentially well for process development, and this resourcefulness may be a significant issue to require membrane processes in most gas separation fields, in a similar way as today membranes represent the main technology for water treatment. This short review emphasizes the mainly promising areas of research in gas separation, by considering the materials for membranes, the industrial applications of membrane gas separations, and finally the opportunities for the integration of membrane gas separation units in hybrid systems for the intensification of processes. Mixed matrix composite (MMC) membranes, incorporating molecular sieving materials within polymeric substrates, may provide economical, high performance gas separation membranes if defects at the molecular sieve/polymer interface can be eliminated.

Index Term-- Fabrication, gas separation, mixed matrix membranes, permeation rate, selectivity

I. INTRODUCTION

Nowadays the cost of energy consumption and environment impact is great concern issue due to rapidly increasing of energy demand and green house gases impact on global climate mitigation. Membrane technology for separating green house gases is likely to play an increasingly important role in reducing the green house gases impact. Membrane separation systems have a low capital cost, compact size, modular configuration, and low specific power consumption, which reduces the production cost [1]. In addition, membrane gas separation is a clean process and requires simple and inexpensive filtration. Among other membrane process, gas separation is also a foremost industrial process, which may perhaps engage enhancement of product streams, recovery of reactants, removal of impurities, and dehumidification of process streams. During the past two decades, separation processes using polymeric membranes have gained considerable potential in industrial applications. The process has several advantages over conventional separation processes, which include cryogenic, solid adsorption, or solvent absorption [2].

The spirit of a membrane development is the membrane itself. Consequently, membrane research is still apprehensive with the development of new techniques and the comprehension of the phenomena in membrane formation across the world. This is due to the difficulties to obtain membranes with the desired properties, i.e., ultra-thin and defect-free dense skin [3]. Different methods of polymer membrane preparation have been covered in several reviews [4]. Generally polymeric membranes fabrication is a complicated process since it involves many steps namely: material selection, drying process, dope solution preparation, casting or hollow fiber spinning, phase inversion process, and post treatment. These steps are illustrated in Fig. 1 [5]. Amongst the various steps, to fully use the growing opportunities in the field of gas separation, strong interest exists in the identification of new membrane materials that can comply with current requirements [5]. Criteria for selecting membrane materials for a given separation are complex particularly when membranes are prepared from glassy amorphous polymers such as polycarbonate (PC) Polyvinylidene fluoride (PVDF), polysulfone (PSf), polyethersulfone (PES), polyimide (PI), polyamide (PA), polypropylene (PP) and polyetherketone (PEK) [6]. Generally, durability, mechanical integrity at the operating conditions, productivity and separation efficiency are important stipulations [6]. Of these requirements, selectivity and permeation rate are the most basic ones. High selectivity and permeability render the operation parameters more flexible (e.g., lower driving force and smaller membrane area to achieve a given separation); therefore, a more efficient separation process results [7].

Inorganic membranes are usually formed from metals, ceramics, or pyrolyzed carbon [8]. Infect the foundation for gas separation was laid by Thomas Graham in 1829, which performed the first recorded experiment on the transport of gases and vapors in polymeric membranes. Early inorganic membranes were developed about 55 years ago [9]. Corning glass developed a homogeneous porous glass (Vycor) with 20-40A˚ pores in the 1940s. Also in the 1940s, membranes were developed by the Manhattan Project to enrich uranium by separating uranium isotopes as UF₆. Inorganic membranes can be divided firstly into dense and porous structures, and for porous membranes into asymmetric and symmetric ones. Typical dense membranes are made of metals (in general palladium, silver and their alloys) or solid electrolytes (such as zirconia) . These membranes are permeable to atomic or ionic forms of hydrogen (Pd layer) or oxygen ( ZrO₂, layer). Porous inorganic membranes are made of oxides (such as alumina, titania, zirconia), carbon, glass or...
metal. Symmetric and asymmetric membranes are defined by the pore structure. Symmetric membranes exhibit homogeneous pore size throughout the membrane (e.g. Glass membrane) [10]. Asymmetric membranes present a change of structure through the membrane. This change can be gradual with conical pore shape, the membranes are called asymmetric. But in most cases, membranes consist of several layers with a pore size reduction in each layer. The multilayer structure prevents the top-layer precursor from penetrating inside the large pores of the support. In some cases, the top layer can be a dense layer. These membranes are called composite membranes [10].

Carbon molecular sieve membranes (CMSMs) are produced by carbonization of a suitable polymeric membrane precursor under controlled conditions. Excellent separation properties of CMSMs have been reported for separation of gas mixtures like natural gas, hydrocarbons, and air [4].

Theory of mixed matrix membranes
Mixed matrix membranes have proven to be effective in separating gas components contained within a gaseous mixture. The mixed matrix membranes typically contain molecular sieves which are embedded within polymeric organic materials. Mixed matrix membranes exhibit the unusual effect that the selectivity of the combined molecular sieves and organic polymer are higher than that of the organic polymer alone. An upper limit for the performance of polymeric membranes in gas separation was predicted by Robeson [10] in early 1990. The performance of various membrane materials available for the separation of O₂/N₂ is depicted in Fig. 1. The figure presents the permeability of the fast gas O₂ on the abscissa on a logarithmic scale and the O₂/N₂ selectivity on the ordinate, again on a logarithmic scale. While the polymer “upper-bound” curve has been surpassed using solid/polymer MMMs, there are still many issues that need to be addressed for large-scale industrial production of these new types of MMMs.

The upper bound trade-off curve still defines the approximate upper bound today, despite intensive theoretical and practical structure-permeability studies [11].

Although molecular sieving materials such as zeolite and carbon molecular sieves (CMS) lie well above the upper bound polymeric trade-off curve and in or near the commercially attractive region, these materials are expensive and difficult to process as membranes. Deficiencies in both the polymeric and purely molecular sieving media suggest the need for a hybrid approach to membrane materials development and material processing. This work considers such a hybrid approach to highlight its potentials and problems that must be overcome to allow its successful implementation [12].

One feature that needs improvement is the excessive thickness of the MMMs. Most of the molecular sieve/polymer MMMs reported in the literature are in the form of thick symmetric mixed matrix dense films with a thickness of about 50 μm and molecular sieve particles with relatively large particle sizes in the micron range have been used. It has been noted that membrane fabrication parameters are of paramount importance. Virtually every environmental factor affects membrane structure, which in turn will influence the permeability, selectivity and other physical properties. A number of variables which influence properties of gas-separation polymers have been proposed [13]. These include polymer type, purity, molecular weight, the ratio of \( M_w \) and \( M_n \), concentration, solvent strength, solvent volatility, solvent type, concentration of residual solvent, environment, temperature of casting surface, and desolvation and relative kinetics, the enriching solvent and its type.

Problem Background of Membrane Fabrication Process
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the development of new techniques and the comprehension of the phenomena in membrane formation across the world. This is due to the difficulties to obtain membranes with the desired properties, i.e., ultra-thin and defect-free dense skin [14]. Different methods of polymer membrane preparation have been covered in several reviews.

Fabrication of Polymer based Membrane

Generally polymeric asymmetric or symmetric membranes fabrication is a complicated process since it involved many steps namely; material selection, drying process, dope solution preparation, casting or hollow fiber spinning, phase inversion process, and post treatment. Fig. 2 illustrated the polymeric membranes preparation process for RO, NF, UF, dialysis, and MF and gas separation. Amongst the various steps, to fully use the growing opportunities in the field of gas separation, strong interest exists in the identification of new membrane materials that can comply with current requirements [5]. Criteria for selecting membrane materials for a given separation are complex particularly when membranes are prepared from glassy amorphous polymers such as polycarbonate (PC) Polyvinylidene fluoride (PVDF), polysulfone (PSf), polyethersulfone (PES), polylimide (PI), polyamide (PA), polypropylene (PP) and polyetherketone (PEK). Generally, durability, mechanical integrity at the operating conditions, productivity and separation efficiency are important stipulations [5, 6]. Of these requirements, selectivity and permeation rate are the most basic ones.

High selectivity and permeability render the operation parameters more flexible (e.g., lower driving force and smaller membrane area to achieve a given separation); therefore, a more efficient separation process results [5, 6].

Much essential research interrelated to the development of polymers with improved tendency to produce hybrid reverse osmosis, gas separation properties core on treatment of penetrant diffusion coefficient via systematic modification of polymer chemical structure or superstructure and either chemical or thermal post-treatment of polymeric membranes [15]. Solubility selectivity may also be increased by modifying polymer structure to increase the solubility of one component in a mixture or adding special agents which can complex with a desired penetrant in a mixture [16].

While inorganic membranes have permselectivities that are five times to ten times higher than traditional polymeric materials and moreover are more stable in aggressive feeds, they are not economically feasible for large-scale applications [15]. Most ceramic, glass, carbon and zeolitic membranes cost between one- and three-orders of magnitude more per unit of membrane area when compared to polymeric membranes and furthermore are difficult to fabricate into large, defect-free areas. An advantage of polymeric materials is that they can be processed into hollow fibers, which offer high separation productivity due to the inherently high surface area to volume ratio. Thus, most commercially available gas separating membranes are still made from polymers despite the limited membrane performance [15].

Fig. 2. Polymeric membranes preparation process for RO, NF, UF, dialysis, MF and gas separation. [5]

Fig. 3. Structure and preparation technique of inorganic membrane. [14]
Fabrication of Inorganic Membrane and Mix Matrix Membrane (MMMs)

Ismail has reviewed inorganic membranes in his paper [14]. According to reviewed paper the inorganic membranes into two major categories based on its structure: porous inorganic membranes and dense (non-porous) inorganic membranes as shown in Fig. 3. Besides that, porous inorganic membranes have two different structures: asymmetric and symmetric. Porous inorganic membranes with pores more than 0.3 nm usually work as sieves for large molecules and particles. Glass, metal, alumina, zirconia, zeolite and carbon membranes are commercially used as porous inorganic membranes. Other inorganic materials, such as cordierite, silicon Carbide, silicon nitride, Titania, mullite, tin oxide and mica also have been used to produce porous inorganic membranes. These membranes vary greatly in pore size, support material and configuration. On the other hand, dense membranes made of palladium and its alloys, silver, nickel and stabilized zirconia have been used or evaluated mostly for separating gaseous components. Application of dense membranes is primarily for highly selective separation of hydrogen and oxygen; transport occurs via charged particles [14].

As mentioned in Fig. 3, Soria [15] has reported about numerous processes can be used to fabrication porous membranes from inorganic materials, the preference of technique depends on the desired material and pore size.

Phase Separation and Leaching

Generally in this process the glass membrane with a symmetric structure (isotropic sponge) of interconnected pores can be prepared by phase separation and leaching techniques [15]. A borosilicate glass (Na2O-B2O3-SiO2) is heated to 550-800°C allowing separating into two phases. One of the phases consists substantially of silicon dioxide which is insoluble in mineral acid. The other phase represents a soluble boric phase rich in alkali. The borate phase is then removed by acid leaching, leaving a porous skeleton of silicon dioxide. This technique can be used to produce either porous glass tubes or hollow glass fibers. The pore size is regulated by the annealing temperature (at constant time and glass composition). Porous glass having a pore size inferior to 2 nm can be produced by this way. But the separation phase is also influenced by the annealing time and/or glass composition, and there are many possibilities for producing glass membranes [15]. The main disadvantage of a porous glass membrane is the instability of the surface. The pore surface is rather active, mainly because of the presence of silanol groups.

Anodic Oxidation

Two types of membrane structure can be obtained:
- Symmetric structure with a network of distinctive conical pores perpendicular to the Surface of the membrane,
- Asymmetric structure with a thick layer of large pores and a thin layer of small pores connected to the large ones.

The process of anodic oxidation of aluminum and the resulting structures which were obtained were described 30 years ago. This method is used to produce the commercial ANOPORE membranes. One side of a thin, high-purity aluminium foil is anodically oxidized in an acid electrolyte, which may contain sulfuric, phosphoric, chromic or oxalic acids. The unoxidised metal remaining on the other side is then removed by dissolution in a strong acid, leaving a regular pattern of pores. The membranes so obtained are not stable under long exposure to water. Their stability can be improved by hydrothermal treatment in water or in a basis. Pore size is determined by the voltage used and by the type of acid [17].

The Fabrication of MMMs Carbon Membranes

In general, the fabrication of carbon membranes involves six important steps, as shown in Fig. 1, however step 1 - 3 has already been described in Fig. 1 respectively [16]. The rest of the steps (step 4-5) are several factors involved that need to be considered in order to ensure the success of each step. Among these steps, the pyrolysis process is the most important step and can be regarded as the heart of the carbon membrane production process. During this stage, the pore structure of the carbon membrane is formed, and this determines the ability of a carbon membrane to separate gases [14, 16].

Pyrolysis

Polymers are coated onto porous supports and then degraded by controlled pyrolysis to produce an inorganic membrane. With this technique, silica membranes are produced from silicone rubber, whereas carbon membranes can be produced from polyacrylonitrile or phenolic resins. This technique is used by Le Carbone Lorraine to produce their carbon membranes [14, 16]. The porous support is formed by carbon fibers obtained by pyrolysis of a 8 mm outer diameter tube. Depending on the pyrolysis degree, the support can be weakly hydrophilic (low temperature) or more hydrophobic (high temperature). One (or two) layer(s) of specific polymer is deposited onto the support surface. The carbon layer is formed by pyrolysis of the polymeric layer in a controlled environment (inert atmosphere). For medium size pores (microfiltration), an organic solution of phenolic resin is deposited onto the support, followed by controlled pyrolysis. To produce smaller pores, a polymeric film is produced by in situ polymerization. The degree of carbonization is controlled by stepped pyrolysis. An inorganic carbon surface is formed and is very stable. Additives, degree and type of pyrolysis control, the pore size is in the range 1 pm down to 2 nm (lab studies).

Particle dispersion and slip casting

Composite ceramic membranes can be prepared by slip casting from particle dispersion. In this method, particles are deposited onto a porous support in one or more layers by dipping or casting (Fig. 4). Particle dispersion can be prepared by mixing, precipitation or crystallization, and/or sol-gel.
The final stage of the process is a strongly interlinked gel network [18-20].

**Chemical vapor deposition**

The selectivity of a carbon membrane may be increased through the introduction of organic species into the pore system of the carbon membrane and their pyrolytic decomposition (i.e., chemical vapor deposition, CVD) [21]. Generally, to manufacture carbon molecular sieves, the inherent pore structure of the carbonaceous precursor is initially tailored into a suitable pore size range by controlling the thermal pretreatment, followed by a final adjustment of the pore apertures by CVD [21].

**CONCLUSION**

All modification brings good effect to the permeation rate and selectivity. There a lot of possibility can happen by modify the original members. In future, all the preparation techniques should be combined in order to get the better membrane for gas separation system. At the moment, the world of gas separation system will move further to the next level of gas separation.

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**Fig. 4. MMMs Carbon membrane fabrication process. [21]**

The slip containing particles, along with organic binders, surfactants, plasticizers flow into the pores of the dry support by capillary suction. The solvent is removed and the particles are retained to form by drying and membrane [18]. Slip casting is probably the most widely used technique for preparing ceramic membranes. Pore size is linked to the dispersed particle size. Membranes with small size pores require very small particles and are prepared by the sol-gel technique. Organic binders allow increasing the strength of the unfired membrane. Plasticizers are added to prevent cracking of the membrane during thermal treatment. Surfactants are used to produce a stable dispersion. Membrane thickness is controlled by dipping time and slip formulation. Pore size depends on the particle size of the slip and the thermal treatment of the layer [14, 16, 17].

**Sol-gel process**

The sol-gel can be divided into two main routes: the colloidal suspension route and the polymeric gel route. In both cases, a precursor is hydrolyzed while a condensation or polymerization reaction occurs simultaneously. The precursor is either an inorganic salt or a metal organic compound. In the colloidal route, a faster hydrolysis rate is obtained by using a water excess. A precipitate of gelatinous hydroxide (or oxhydroxide) particles is formed and then peptized to give a stable colloidal suspension. By different processes, this suspension is transformed in a gel structure consisting of a network of particles or agglomerate chains. In the polymeric gel route, the hydrolysis is kept low by using a lack of water.
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