

Chapter 2

Fundamentals of Membrane Processes

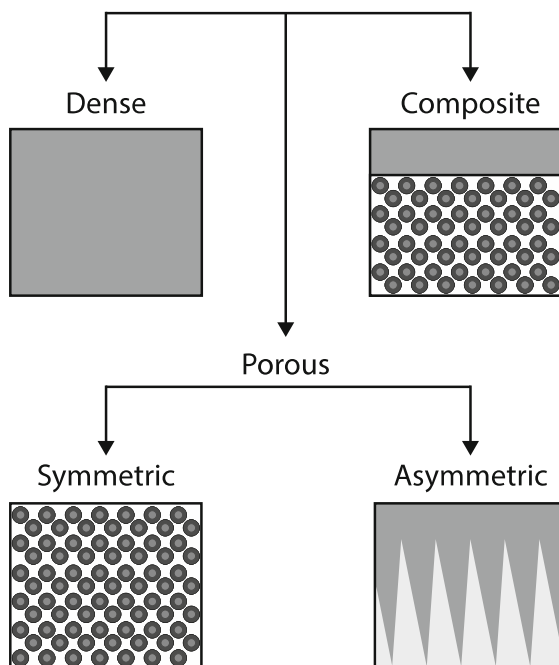
In this chapter the common fundamentals of different membrane processes are described. In the first part a general description of the different membrane structures, such as porous and dense homogeneous or symmetric and asymmetric membranes, and their function is discussed. In the second part membrane materials such as inorganic, organic, and composite materials and their function in membrane bioreactors are described. Third, the preparation of synthetic membranes via the phase inversion method is described in detail. Finally, alternative techniques of membrane fabrication are presented.

2.1 Membrane Classification by Membrane Structure

Synthetic membranes display a broad range in their physical structure and the material they are made from (Strathmann 2011). They can be classified according to their morphology, as shown in Fig. 2.1.

The first group is dense homogeneous polymer membranes. Usually they are prepared (i) from solution by solvent evaporation only or (ii) by extrusion of the melted polymer (Nunes and Peinemann 2006). However, dense homogeneous membranes only have a practical usefulness when they are made from a highly permeable polymer such as silicone. Commonly, the permeate flow across the membrane is quite low, since a minimal thickness is required to grant the membrane mechanical stability. The majority of membranes currently are porous or consist of a dense top layer on a porous structure (Mulder 1984, 1997; Nunes and Peinemann 2001; Strathmann et al. 2006).

Fig. 2.1 Membrane classifications according to morphology. Adapted from Nunes and Peinemann (2006)



The second category is porous membranes, which can also be divided into two main groups. They are divided according to their pore diameter: microporous ($d_p < 2$ nm), mesoporous (2 nm $< d_p < 50$ nm) and macroporous ($d_p > 50$ nm) (Gallucci et al. 2011b).

The first groups of membranes are referred to as symmetric (isotropic) and the second type is referred to as asymmetric (anisotropic) membranes. Within the asymmetric membranes, there are several distinctly different structures including integrally skinned membranes (where the pore structure gradually changes from very large pores to very fine pores, essentially forming a “skin” on top of the membrane, giving rise to the name “integrally skinned”). Alternatively, the skin may be nonporous. A third, and industrially very important type of asymmetric membrane is the thin-film composite membrane, where a dense, selective, thin layer is deposited or polymerised at the surface/interface of a porous substrate.

Symmetric membranes refer to the membranes with uniform structure (uniform pore size or nonporous) throughout the entire membrane thickness (Buonomenna et al. 2011). Symmetric membranes are used today mainly in dialysis, electro-dialysis, and to some extent also in microfiltration (Strathmann 2000, 2011). The thickness of symmetric membranes is usually between 30 and 500 μ m. The total resistance of the mass transfer relies on the total thickness of the membranes. Hence, a decrease in membrane thickness results in an increased permeation rate.

Asymmetric membranes have a gradient in structure. They consist of a 0.1–5 μm thick “skin” layer on a highly porous 100–300 μm thick structure (Strathmann 2011). The skin represents the actual selective barrier of the asymmetric substructure. Its separation properties are thoroughly determined by the nature of the material or the size of pores in the skin layer. The porous substrate layer serves as a support for the mostly very thin top layer, or “skin” (relatively dense) and has little effect on the separation properties of the membrane or the mass transfer rate of the membrane (Strathmann 2011). The dense surface layer is considered to be responsible for the membrane selectivity. Consequently, the controlled structure of the dense surface layer has become a serious concern in the membrane design (Zhenxin and Matsuura 1991). Also, the resistance to the mass transfer is mainly determined by the top layer (Buonomenna et al. 2011; Nunes and Peinemann 2001). Asymmetric membranes are primarily employed in pressure driven membrane processes such as reverse osmosis, ultrafiltration, gas separation and sometimes in microfiltration. High fluxes (high permeate flow per unit area), a reasonable mechanical stability providing very thin selective layer are the unique properties of asymmetric membranes (Strathmann 2011; Nunes and Peinemann 2006). Two procedures are used to prepare asymmetric membranes: the first method is based on phase inversion process which leads to integral structure (Kesting 1971), The second method resembles a composite structure in a two-step process in which a thin barrier layer is deposited on a microporous substructure (Cadotte and Petersen 1981; Strathmann 2011).

2.2 Membrane Materials

In general, there are three fundamentally different categories of membrane materials: Organic (polymeric), inorganic (ceramic) materials and biological materials. Organic materials are either cellulose—based or composed of modified organic polymers. By contrast, inorganic materials such as ceramics and metals are used in niche industrial applications but are usually cost-prohibitive in wastewater treatment. Biological membrane (bio membranes) is a selective barrier within or around a cell in a living organism. The biomembrane is capable of recognising what is necessary for the cell to receive or block for its survival. These membranes cannot meet the industrial requirements due to thermomechanical stability and productivity. It should be pointed out that, a large majority of membranes in research and commercial use are polymeric-based (organic membrane) as a result of their facile processing into viable membrane structures and the diverse polymers available, as well as the capability to synthesise novel polymer structures (Peyravi et al. 2012). Recently, composite membranes and inorganic membranes have gained tremendous attention owing to their potentially high performance, long lifetime and even their availability that outweigh the benefits/advantages of using polymeric membranes.

2.2.1 Inorganic Membranes

Inorganic membranes possess excellent thermal and chemical stability in comparison to polymeric membranes and have higher antifouling property due to the hydrophilic nature of inorganic material (Gallucci et al. 2011a; Mulder 1997). Nevertheless, there has been some limitation in their use despite their wide use and application. The main application of inorganic membranes in the past was enrichment of uranium hexafluoride U^{235} via Knudsen flow through porous ceramic membranes. Recently, many more applications are found in the field of ultrafiltration and microfiltration. Inorganic membranes are generally divided into four groups: glass membranes, ceramic membranes, metallic membranes, carbon membranes, and zeolitic membranes.

Metallic membranes can generally be obtained via the sintering of metal powders (e.g. stainless steel, molybdenum, or tungsten). According to (Gallucci et al. 2011a), the main materials for preparing metallic membranes are palladium and its alloys due to their high solubility and permeability of hydrogen. These membranes are employed for separation of hydrogen from gas mixtures and in the membrane reactor area for producing pure hydrogen (Lin 2001). These membranes have both advantages and disadvantages. The advantages are considerable mechanical strength and higher permeating flux (Gallucci et al. 2011a). The limitations of metallic membranes are (1) highly cost (very expensive) due to the low availability of palladium in nature and (2) surface poisoning, which is significantly more for thin metal membranes. There have been numerous studies reporting that the impact of poisons such as CO or H_2S on Pd-based membranes is a major problem. These gases (H_2S or CO) adsorb on the palladium surface that block the dissociation sites for hydrogen. Therefore, these membranes have received limited attention today because they do not relate to MBR technology (Judd 2006).

Ceramic membranes are of great importance in separation technology as they have a higher chemical, thermal and mechanical stability compared to organic membranes (Belfer et al. 2000). This stability makes these UF or MF membranes suitable in different fields of industry such as (food, biotechnology and pharmaceutical applications). They have been proposed for gas separation and the application of membrane reactor. Ceramic membranes are prepared through the combination of a metal (e.g. aluminium, titanium, silicon or zirconium, zinc, tin, and iron) with a non-metal in the form of oxide, nitride, or carbide to form a variety of inorganic nanoparticles (fillers) such as carbon nanotubes, alumina, or aluminium oxide (Al_2O_3), titanium oxide (TiO_2), zirconium dioxide or zirconia (ZrO_2), zinc oxide (ZnO), Silver, tin oxide (SnO_2), and Fe_3O_4 . All these membranes have been used to fabricate inorganic–polymer composite membranes (Arthanareeswaran et al. 2008; Huang et al. 2006; Jian et al. 2006; Liang et al. 2012; Yang et al. 2007; Zoppi and Soares 2002; Leo et al. 2013; Celik and Choi 2011; Celik et al. 2011a, b; Bae and Tak 2005a, b; Maximous et al. 2010; Gallucci et al. 2011a; Leo et al. 2012; Lu et al. 2005; Mulder 1997; Rahimpour et al. 2008, 2009; Razmjou et al. 2011a, b; Sawada et al. 2012; Yu et al. 2009a, b; Livari et al. 2012; Moghimifar et al. 2014). Sintering or sol–gel techniques are usually used to prepare ceramic membranes.

Glass membranes can be regarded as ceramic membranes. Issues associated with ceramic membranes are the difficulties faced in proper sealing of the membranes in modules operating at high temperature, extremely high sensitivity of membranes to temperature gradient, leading to membrane cracking, and chemical instability of some perovskite-type materials (Gallucci et al. 2011a). Glass membranes (silica, SiO₂) are generally prepared by leaching techniques.

Carbon membranes (also called carbon molecular sieve membranes CMS) have been regarded as a promising candidate for applications of gas (Gallucci et al. 2011a). CMS are porous solids membranes, containing constricted holes that are responsible for approaching the molecular dimensions of diffusing gas molecules. Therefore, molecules with different size can be efficiently separated through molecular sieving (Gallucci et al. 2008). CMS membranes can be prepared by pyrolysis of thermosetting polymers such as poly acrylonitrile (PAN), cellulose triacetate, phenol formaldehyde, and poly (furfural) alcohol.

Recently, a new class of membranes have been developed and studied, such as the zeolitic membranes. These membranes have a very narrow pore size and can be employed in gas separation, pervaporation and separation of ions from aqueous solution by reverse osmosis. These membranes have some limitations; first the main limitation is relatively low gas fluxes in comparison to other inorganic membranes. Second, its thermal effect, as noted by Cejka et al. (2007), the zeolite layer exhibits negative thermal expansion, in which the zeolite layer shrinks when the region temperature is high, but the support layer expands continuously, causing thermal stress issues for the attachment of the zeolite layer to the support and for the connection of the individual microcrystals within the zeolite layer.

Inorganic membranes have both advantages and disadvantages as presented in Table 2.1. The major advantages of inorganic membranes when compared with polymeric membranes, is their high chemical, thermal, and mechanical stability and wide tolerance to pH (Belfer et al. 2000; Gallucci et al. 2011a). They can operate at high temperatures. As a fact of matter, inorganic membranes are stable at

Table 2.1 Advantages and disadvantages of inorganic membranes with respect to polymeric membranes (Gallucci et al. 2011a)

Advantages	Disadvantages
1. Long-term stability at high temperatures	1. High capital cost
2. Resistance to harsh environments (e.g. chemical degradation, pH, etc.)	2. Embrittlement phenomenon (in the case of dense Pd membranes)
3. Resistance to high pressure drops	3. Low membrane surface per module volume
4. Inertness to microbiological degradation	4. Difficulty of achieving high selectivities in large-scale microporous membranes
5. Easy cleanability after fouling	5. Low permeability of the highly hydrogen selective (dense) membranes at low temperatures
6. Easy catalytic activation	6. Difficult membrane to module sealing at high temperature

temperatures ranging from 300 to 800 °C and in some cases, ceramic membranes usable over 1000 °C (van Veen et al. 1996). They also have a high resistance to chemical degradation. Judd et al. (2004) stated that ceramic membranes did not foul substantially at fluxes up to 60 L m⁻² h⁻¹, whilst polymeric membranes fouled at a lower flux of 36 L m⁻² h⁻¹. Applicability of inorganic membranes is of great interest in non—aqueous filtration due to stability in organic solvents (Tsuru et al. 2000a, b). Despite their potential in waste water treatment, certain limitations deter membrane processes from large scale and continuous operation (Lee et al. 1999). One of the major limitations arises from membrane fouling caused by different inorganic salts (Bhattacharjee and Johnston 2002) which increases feed pressure, reduces permeate flux, decreases product quality and finally shortens membrane lifespan (Lee and Lee 2000; Seidel and Elimelech 2002).

Another limitation of inorganic membranes that probably hampers their application is the high capital costs of both the manufacturing process and material (Gallucci et al. 2011a). Therefore, the inorganic membranes might be used only in some special applications such as anaerobic biodegradation (Fan et al. 1996) and high temperature waste water treatment (e.g. high-strength industrial waste) (Luonsi et al. 2002; Scott et al. 1998). Despite, the high expense of inorganic membranes and their susceptibility to membrane fouling, they are still a competitive product in many applications. It is expected that inorganic membranes will have more applications in the future. Table 2.1 summarises the advantages and disadvantages of inorganic membranes over polymeric membranes.

2.2.2 *Polymeric Membranes*

Although polymer membranes are less resistance to high temperature and aggressive chemicals than inorganic or metallic membranes, they are still the most widely used materials in wastewater treatment applications. This is mainly owing to easy preparation, reasonable expense (low cost), high efficiency for removing dispersed oil, particles, and emulsified, small size, lower energy requirement, flexibility in membrane configuration, and relatively low operating temperature which is also associated with less stringent demands for the materials need in the construction of module (Buonomenna et al. 2011; Nunes and Peinemann 2010). Among many homopolymeric materials presented in Table 2.1, polyethersulfone (PES) is one of the most vital polymeric materials and is widely used in producing microfiltration (Li et al. 2008, 2009a, b; Ulbricht et al. 2007; Zhao et al. 2003a, b; Shin et al. 2005; Liu and Kim 2011), ultrafiltration (Chaturvedi et al. 2001; Marchese et al. 2003; Xu and Qusay 2004; Wang et al. 2006a, b, c) as well as nanofiltration membranes (Boussu et al. 2006; Ismail and Hassan 2007), either on the laboratory or industrial scale (Razali et al. 2013) Polyethersulfone (PES) has been recognised or acknowledged as a high performance polyaromatic polymer possessing toughness and thermal stability (Huang et al. 2012; Li et al. 2004; Shi et al. 2008; Shin et al. 2005; Zhao et al. 2013).

PES is a thermoplastic polymer and is typically amorphous in nature and shows one prominent XRD peak at $2\theta = 19.9^\circ$ (Nair et al. 2001; Kumar et al. 2006; Guan et al. 2005). PES membranes show a high glass transition temperature ($T_g \approx 503$ K). PES structure has a harder benzene ring and a softer ether bond; so crystalline properties can be expected (Barth et al. 2000; Ismail and Hassan 2007). Additional properties include

- Good chemical resistance (inertness): PES exhibits excellent chemical resistance to aliphatic hydrocarbons, alcohols, and acids. It is also soluble in some aprotic polar solvents (Zhu et al. 2014).
- Blood compatibility.
- Outstanding oxidative stability.
- Outstandingly high mechanical strength.
- Easy processing and environmental endurance.
- Wide temperature and pH tolerance.
- Moderate good chlorine resistance.
- Easy to fabricate membranes in a wide variety of modules and configurations as well as wide range of pore size available for UF and MF from 10 A to 0.2 μm .
- PES also shows other good qualities such as good membrane forming properties.
- Commercially available and relatively inexpensive (Bolong et al. 2009).

Polyethersulfone has been affirmed as the membrane material in many processes such as in biomedical fields for blood purification (haemodialysis and plasma collection) (Barzin et al. 2004; Samtleben et al. 2003; Tullis et al. 2002; Werner et al. 1995; Zhao et al. 2001; Unger et al. 2005), hollow fibres (Khulbe et al. 2003) (Yang et al. 2007), stable substrate for the deposition and thermal processing of semiconductor thin films (Nair et al. 2001), sensors applications (Gerlach et al. 1998), sterilisation and pharmaceutical (Baker 2012; Song et al. 2000), water purification, beverage filtration, protein separation, and pre-treatment of reverse osmosis (Bolong et al. 2009; Yu et al. 2011).

However, its main limitations is related to the relatively high hydrophobic property, which can lead to severe membrane fouling (Kim et al. 1999; Van der Bruggen et al. 2002a, b) owing to the adsorption of nonpolar solutes and hydrophobic particles or bacteria onto its surface (Khulbe et al. 2000, 2010; Koh et al. 2005; Rahimpour and Madaeni 2010). This would lead to the gradual reduction of permeation flux, frequent membrane cleaning, impacting on the useable lifetime of the membrane and its applications (Daraei et al. 2013a, b, c; Luo et al. 2005; Yamamura et al. 2007a, b; Zhao et al. 2013; Rahimpour et al. 2011). Therefore, achieving the desired surface properties without modification of the advantageous properties of PES membrane is a paramount goal for membrane researchers and industry.

Regarding of the preparation of PES membranes, (Zhao et al. 2013) stated that the structure of PES membranes is always symmetric and is prepared by phase inversion methods. The structure of PES membrane is affected by the composition

(e.g. concentration, solvent, and additives), temperature of PES solution, the non-solvent or the mixture of nonsolvents, and the coagulation bath or even the environment (Barth et al. 2000).

Many other polymeric materials can also be employed for fabricating membranes as explained schematically in Table 2.2. This table illustrates some examples of polymeric materials used for microfiltration, ultrafiltration, reverse osmosis, and some membrane processes.

Recently, copolymer is another important polymeric material in the manufacture of membranes. It is gaining more attention by a number of researchers. The copolymers are composed of at least two different types of structural units with different properties. The properties of copolymers rely on the properties of the units that are connected in the polymer and their relative proportions. Hence, polymers that are employed for the preparation of membrane and require different properties can be copolymerised carefully by selecting various polymeric units. To date, many membranes with high performance have been fabricated by different copolymers with different molecular structures (for example, block copolymers: poly (ethylene oxide)–polysulfone block copolymer (Hancock et al. 2000), graft copolymers: poly (ethylene glycol)-graft-polyacrylonitrile copolymer (Su et al. 2009b), and so on.

2.2.3 Composite Membranes

Composite membranes are often referred to as thin-film composite (TFC) membranes and they have received tremendous attention in recent years for desalination of brackish and sea water, waste water reclamation, and the separation and purification of chemical and biological products (Buch et al. 2008). TFC membranes are composed of at least two layers (with different (polymeric) materials), with a very selective membrane material being deposited as a dense ultrathin layer formed upon a more or less porous support layer (sublayer), which usually is an ultrafiltration membrane and serves as support as shown in Fig. 2.2 (Strathmann 1989; Wu 2012). The advantage of TFC membranes is each layer (i.e. top selective layer and bottom porous substrate) is thoroughly optimised and controlled independently to achieve the desired selectivity and permeability while presenting excellent compression resistance and mechanical strength (Jahanshahi et al. 2010; Lau et al. 2012; Rahimpour 2011; Kosaraju and Sirkar 2008). The porous support layer (bottom layer) is generally prepared through phase inversion method. On the other hand the top selective layer is prepared from elastomer, which is hard to prepare it through phase inversion method. The first generation TFC membranes were prepared by pouring a thin layer of polymer solution on a liquid of water or mercury (Mulder 1997). Numerous coating procedures have been used to prepare TFC membranes, including plasma polymerisation, dip coating, in situ polymerisation, and interfacial polymerisation. These techniques will be discussed in this chapter.

Table 2.2 Overview of polymeric materials used for membranes, the type of membranes formed and the membrane processes they are used in Ulbricht (2006)

Polymer	Barrier type	Morphology cross section	Barrier thickness (µm)	Membrane processes
Cellulose acetates	Nonporous	Anisotropic	~0.1	GS, RO
	Mesoporous	Anisotropic	~0.1	UF
	Macroporous	Isotropic	50–300	MF
Cellulose Nitrites	Macroporous	Isotropic	100–500	MF
Cellulose regenerated	Mesoporous	Anisotropic	~0.1	UF, D
Perfluorosulfonic acid polymer	Nonporous	Isotropic	50–500	ED, fuel cell
Polyacrylonitrile	Mesoporous	Anisotropic	~0.1	UF
Polyetherimides	Mesoporous	Anisotropic	~0.1	UF
Polyethersulfone	Mesoporous	Anisotropic	~0.1	UF
	Macroporous	Isotropic	50–300	MF
Polyethylene terephthalate	Macroporous	Isotropic track-etched	6–35	MF
Polyphenylene oxide	Nonporous	Anisotropic	~0.1	GS
Polytetrafluoroethylene	Macroporous	Isotropic	50–500	MF
	Nonporous	Isotropic	~0.1	GS
Polyamide, aliphatic	Macroporous	Isotropic	100–500	MF
Polyamide, aromatic	Mesoporous	Anisotropic	~0.1	UF
Polyamide, aromatic, In situ synthesised	Nonporous	Anisotropic/composite	~0.05	RO, NF
	Macroporous	Isotropic track-etched	6–35	MF
Polycarbonates, aromatic	Macroporous	Isotropic track-etched	6–35	RO, NF
	Nonporous	Anisotropic/composite	~0.05	RO, NF
Polyether, aliphatic crosslinked, In situ synthesised	Macroporous	Isotropic	50–500	MF
Polyimides	Nonporous	Anisotropic	~0.1	GS, NF
Polypropylene	Macroporous	Isotropic	50–500	MF

(continued)

Table 2.2 (continued)

Polymer	Barrier type	Morphology cross section	Barrier thickness (μm)	Membrane processes
Polysiloxanes	Nonporous	Anisotropic/composite	$\sim 0.1 < 1-10$	GS, PV, NF (organophilic)
Polysulfone	Nonporous Mesoporous	Anisotropic Anisotropic	~ 0.1 ~ 0.1	GS UF
Polyvinyl alcohol, crosslinked	Nonporous	Anisotropic/composite	$< 1-10$	PV (hydrophilic)
Polyvinylidene fluoride	Mesoporous Macroporous	Anisotropic Isotropic	~ 0.1 50-300	UF MF
Poly(Styrene-co-divinylbenzene), sulfonated or terminated	Nonporous	Isotropic	100-500	ED

RO reverse osmosis, *NF* nanofiltration, *UF* ultrafiltration, *MF* microfiltration, *GS* gas separation, *ED* electrodialysis, *PV* pervaporation

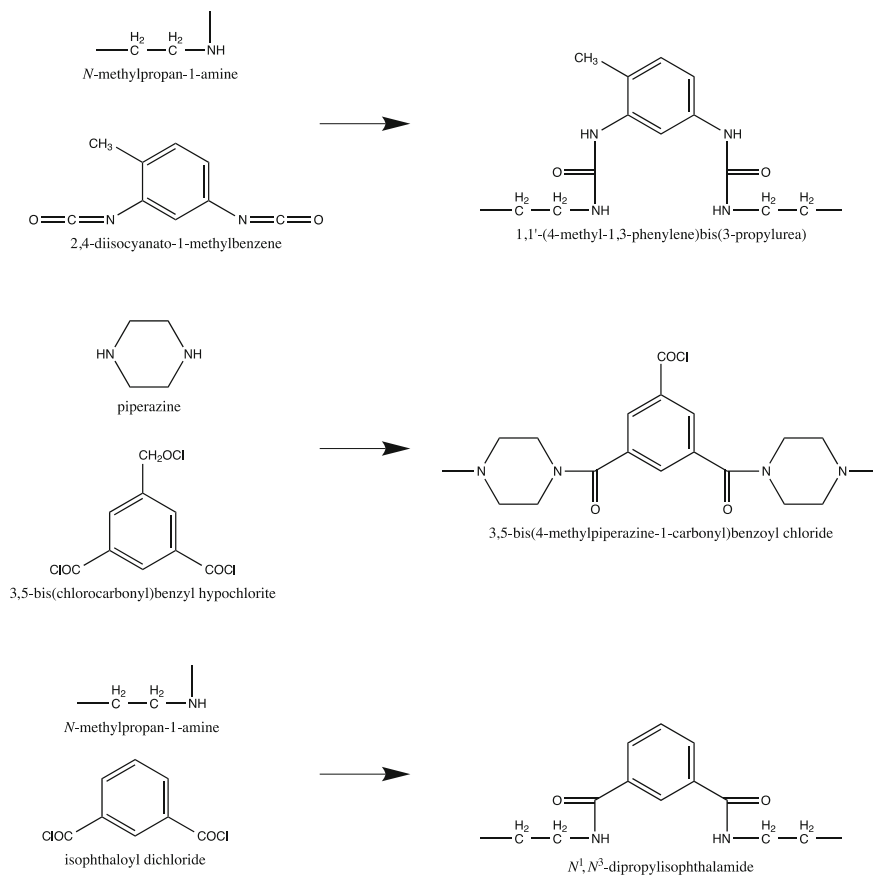


Fig. 2.2 Examples of the preparation of composite membranes by interfacial polymerization (Mulder 1997)

Another type of procedure used to prepare composite membranes, is the coating layer, which plugs the pores in the sublayer. In this procedure, the unique characteristics of the sublayer compared to those of the coating layer highlight the overall properties. With other techniques like stretching, sintering, leaching out and track-etching, porous membranes can be obtained. Porous membranes are mainly used as sublayer for composite membranes. Using phase inversion method is frequently possible to obtain open or dense structures. Various techniques have been implemented to prepare the ultrathin barrier layer upon the supporting layer. These techniques include (Lau et al. 2012; Mulder 1997; Seman et al. 2012).

- (a) Interfacial polymerization (IP): It is a technique that is used for depositing the thin selective layer onto the porous layer. Polymerisation reactions emerge between two reactive monomers that react on the interface of two immiscible phase (an aqueous phase and an organic solvent such as hexane) through

interfacial polymerization, and form a denser polymeric top layer on the supporting layer surface. The benefits of this technique are self-inhibiting through passage of a limited supply of reactants through the already formed layer, causing an extremely thin film of thickness in the range of 50 nm. Figure 2.2 illustrates some examples of monomers and pre-polymers that can be used to prepare composite membranes by interfacial polymerization.

- (b) Dip coating: It is a straightforward and effective technique to prepare composite membranes with a very thin structure but dense toplayer. Membranes obtained by this technique can be used in gas separation, pervaporation and reverse osmosis applications. The principle of this method is dip coating a polymer solution onto the supporting layer's surface and then drying the coated layer (using oven).
- (c) Lamination: In this technique, casting an ultrathin layer and then the microporous layer is covered with the casted ultrathin layer.
- (d) Plasma-initiated polymerization: This technique involves depositing the barrier film directly on the microporous support layer by gaseous phase monomer plasma using an electrical discharge at high frequencies up to 10 MHz (Mulder 1997).

2.2.4 Formation of Membranes by Phase Inversion Method

Generally, various techniques have been extensively used to prepare synthetic membranes either inorganic membranes (e.g. ceramics, metals, glass, Zeolites) or organic membranes that includes all sorts of polymers (Mulder 1997; Nunes and Peinemann 2006; Strathmann et al. 2006). The purpose of preparation is to modify the material using an appropriate technique to obtain a membrane structure with an appropriate morphology for a specific separation. The preparation method is limited by the materials used, the membrane morphology obtained and the separation principle applied.

The techniques that are being employed for the preparation of synthetic membrane are phase inversion, stretching of films, irradiation and etching of films, sintering of powders, track-etching, sol-gel process, microfabrication vapour deposition and coating (Hoek and Elimelech 2003; Hoek et al. 2002; Jeong et al. 2007; Mulder 1997; Tang et al. 2008; Ulbricht 2006). One of the most important methods is phase inversion.

Phase inversion method is arguably one of the most common and versatile technique used to prepare all sorts of morphologies (both symmetric and asymmetric types) due to the significance of immersion precipitation (Boom et al. 1992; Buonomenna et al. 2011; Madaeni and Rahimpour 2005a, b; Mulder 1997; Rahimpour and Madaeni 2010; Rahimpour et al. 2007a, b, 2009, 2010a, b). It is a process whereby a polymer is transformed in a controlled manner from a liquid state to a solid state. Throughout this technique, a thermodynamically stable

polymer solution with a multiple components is subjected to a liquid–liquid demixing whereby the cast polymer film separates into a polymer–rich phase (membrane matrix) and a polymer–lean phase (membrane pores) (Buonomenna et al. 2011). The mechanism of phase inversion during membrane formation can be concisely described by a polymer/solvent/nonsolvent system, as explained typically by a ternary phase diagram shown in Fig. 2.3 (Buonomenna et al. 2011).

The corners of the triangle act the three components (polymer, solvent, non-solvent), whilst at any point within the triangle represents a mixture of three components (starting compositions of the casting solution); the binodal curve divides the triangle into two phase regions; a one-phase region where all components are miscible to and a two-phase region where the system is separated into a polymer-rich, generally a solid phase and a polymer-poor which is generally liquid phase (although the one-phase region in the phase diagram is continuous thermodynamically).

For practical purposes it can conveniently be divided into a liquid and a solid region. The tie lines within the two-phase region connect two equilibrium states on the binodal curve, which also represent the compositions of two coexisting phases generated during the phase separation. The region between the spinodal and the binodal curves is called metastable region, where phase separation appears under certain initiation (nucleation). The region within the spinodal curve corresponds to unstable composition where immediate demixing occurs after entering this region.

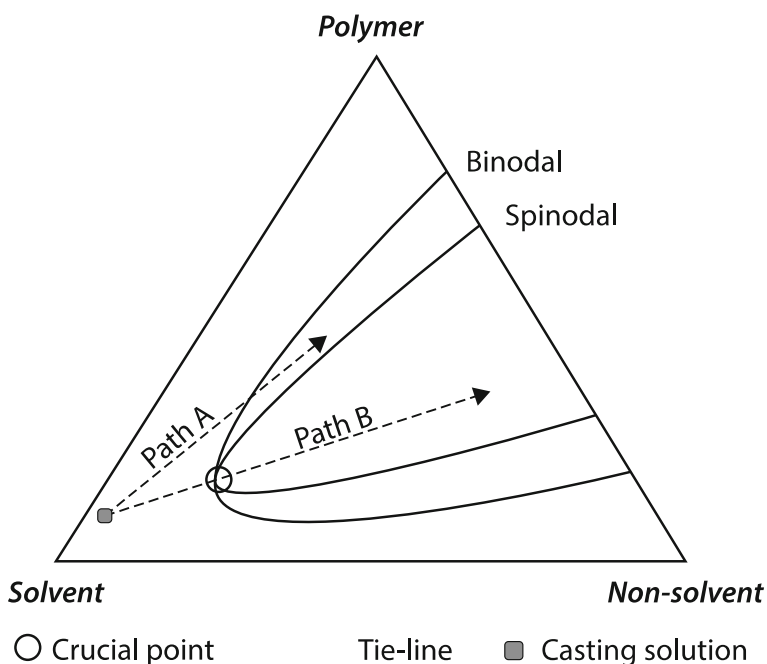


Fig. 2.3 Ternary phase diagram (solvent/polymer/nonsolvent) for membrane formation via phase inversion process (Machado et al. 1999)

By immersing a thin layer casting solution into a coagulation bath, the solvent of the casting solution is exchanged with a nonsolvent (Rahimpour and Madaeni 2007). The composition of the coagulation and casting solution are the most considerable factor, as it determines the phase inversion path of a membrane forming system (Albrecht et al. 2001).

The filled square represents the initial state of casting solution. The exchange between solvent and nonsolvent changes the composition in the casting film. Once demixing polymer solution arrives in the metastable region between the binodal and the spinodal, the region is referred to “binodal demixing” and therefore represents path A (Fig. 2.3). In this region, the polymer solution is separate into a polymer-lean phase and a polymer-rich phase (Buonomenna et al. 2011). Another pathway towards miscibility gap (path B) is called “spinodal decomposition”. In this pathway, the composition path passed through the thermodynamically unstable zone (critical point), in which the binodal and spinodal curve converge, and two co-continuous phases formed. This process yields asymmetric membranes with a dense top layer and porous sublayer containing macrovoids, pores, and micropores (Rahimpour and Madaeni 2007).

The general concept of phase inversion method covers a variety of different techniques, including:

- (a) **Precipitation by solvent evaporation:** Precipitation by solvent evaporation is a straightforward technique used to prepare phase inversion membranes. The polymer is dissolved in a solvent and form homogenous solution (casting or dope solution). Then, the dope solution is casted on a suitable support (e.g. glass plate) or another type of support that may be nonporous (polymer) or porous (non-woven fabric). Later, the solvent is allowed to evaporate in an inert gas (e.g. nitrogen) to exclude water vapour, allowing a dense homogeneous membrane to be obtained (Mulder 1997).
- (b) **Precipitation by controlled evaporation:** In the early years this technique has been used. In this method, the polymer is dissolved in a mixture of solvent and nonsolvent. Even though, the solvent is more volatile than the nonsolvent, the evaporation step leads to polymer precipitation own to higher nonsolvent content. The structure of membrane prepared by this technique is skinned membranes.
- (c) **Thermal precipitation:** Polymeric solution in a mixed or single solvent is cooled to allow phase separation to occur. Evaporation of the solvent usually allows the formation of a skinned membrane (Cheryan 1998; Oh et al. 2009; Su et al. 2009a, b). This method is thoroughly used to prepare microfiltration membranes.
- (d) **Precipitation from the vapour phase:** In this method, a dope solution, which consists of a polymer and a solvent, is placed in a vapour atmosphere whereas vapour phase consists of a nonsolvent saturated with the same solvent. The high solvent concentration in the vapour phase prohibits the evaporation of solvent from the cast film. As a result of diffusion of nonsolvent into the cast film, the membrane formation appears. This leads to formation of porous membrane without a top layer.

- (e) Immersion precipitation or nonsolvent induced phase inversion: This is one of the most common methods in the preparation of the most polymeric micro-filtration and ultrafiltration and some of nanofiltration which is used for separation processes (Ismail and Hassan 2007). In this procedure, a film of homogenous polymeric solution is cast on a suitable substrate after preparing it by dissolving polymer into solvent. Then the cast film is immersed in a coagulation bath containing deionised water or methanol. Precipitation occurs as a consequence of the exchange between the solvent and nonsolvent. The membrane structure essentially is obtained from a combination of mass transfer and phase separation method (Rahimpour et al. 2010a). Keeping in mind, that thermodynamic behaviour of a polymer solution is attributed to immersion—precipitation and is represented by polymer/solvent/nonsolvent systems (Buonomenna et al. 2011). This precipitation is also called dry/wet method (Zhao et al. 2008; Oh et al. 2009).

2.3 Membrane Fabrication Techniques

Membranes of different arrangements are formed in order to meet different industrial and domestic demands; thus, various casting techniques have been implemented to obtain different types of the membrane such as flat sheet membrane (casting), hollow fibre membrane (spinning) and composite membrane (dip coating). The first two, will be discussed in this chapter. The third one is discussed previously.

2.3.1 Flat Sheet Membranes

For research purposes, flat sheet membrane is a relatively simple method used to fabricate/prepare membranes. In industrial scale, the casting method employed is usually a continuous mode as shown below in Fig. 2.4 (Mulder 1997).

The principle of this method is the polymer is initially dissolved in an appropriate solvent mixture (which may include additives) and forms a homogeneous (dope) solution. Molecular weight of a polymer, concentration of the polymer and the kind of solvent used (mixture) are three factors (parameters) affect the viscosity of the dope solution. Afterward, the polymer solution is spread (poured) and cast directly to a thin film of a homogenous polymer solution using one of the supporting layer (for example, clean glass plate, or polyethylene non-woven fabric, polyester, metal, and Teflon) by means of steel casting knife and adjusting the thickness of the membranes. The casting thickness can roughly vary from 50 to 500 μm . The thin film of a homogenous polymer solution (protomembrane) is immediately immersed in a second liquid, which is a nonsolvent for the polymer;

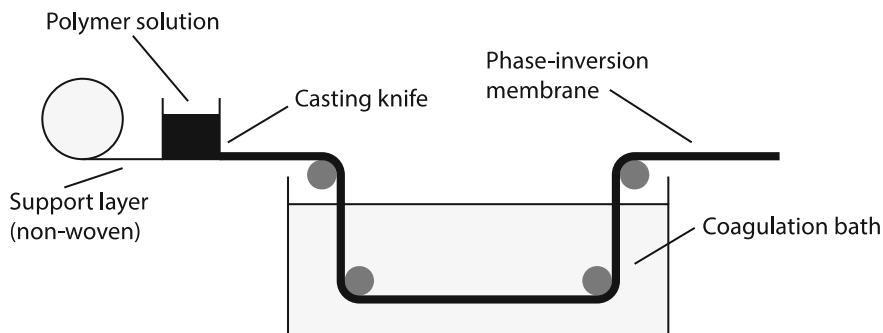


Fig. 2.4 Schematic of continuous flat sheet membrane preparation. Adapted from Mulder (1984, 1997)

however, it is miscible with the polymer solvent. Exchange between the solvent and nonsolvent occurs and ultimately introduces phase separation in polymer film and would lead to the formation of membranes (Rahimpour and Madaeni 2010; Rahimpour et al. 2010a, b; Mulder 1997). Water is used as a nonsolvent (second liquid), as it is a powerful nonsolvent. Organic solvents (e.g. methanol) can be used for the same purpose as well. Since the solvent/nonsolvent pair is a very important characteristic in obtaining the desired structure, the nonsolvent cannot be chosen at will.

A non-continuous mode is usually employed in a laboratory scale. The three-component polymer solution (polymer/solvent/additive) is prepared and stirred under particular temperatures in order to ensure complete dissolution of the polymer. After the polymer solution is placed for some time and the complete release of bubbles is confirmed, the homogenous solution is cast on glass plates using a casting knife with a specific thickness (for example, filmographe Dr. Blade 150 μm ; Erichsen blade 150 μm). This is immediately moved to the coagulation bath (which is usually deionised water) for immersion at room temperature without any evaporation. Then, the membranes are peeled off the glass and subsequently rinsed with deionised water and stored in fresh deionised water for at least one day to leach out all residual solvents (Rahimpour and Madaeni 2010; Rahimpour et al. 2009, 2010a, b). At the final stage, membrane is sandwiched by placing between two sheets of filter paper or placing in air for 24 h at room temperature.

In Summary, flat sheet membranes are relatively straightforward to prepare, as they are very effective for characterising on laboratory scale. A dead end cell station is usually used for measuring water flux of membranes.

For very small membrane surface area (less than 1000 cm^2), the membranes are mostly cast by hand or semi-automatically using glass plate, not on non-woven polyester.

2.3.2 *Hollow Fibre Membranes*

Spinning is another technique used to prepare hollow fibre membranes. For industrial applications, hollow fibre membranes are more applicable, more effective and cheaper than flat sheet membranes because hollow fibre membranes have relatively higher (surface/volume) ratio compared to flat sheet membranes, which can have a greater resistance to pressure. Additionally very few manufactures supply flat sheet membranes (Zhao et al. 2013). Hollow fibre membranes have a minimum dead space; therefore it can be physically cleaned by frequent backwash, yielding longer life to the membranes. It has been designed with specific dimensions that are suitable to minimise membrane fouling in a given application. Many scholars believe that hollow fibre membranes and flat membranes can exhibit similar performance. But, the procedures for their preparation are thoroughly different, considering hollow fibre membranes are self-supporting. The fibre dimensions are a paramount aspect and should be taken into account when preparing hollow fibre membranes.

In general, hollow fibre membranes can be prepared by three methods:

- (a) Wet spinning method: possible but rarely used to prepare hollow fibre membranes,
- (b) Melt spinning, and
- (c) Dry spinning (dry-wet spinning): this method is more applicable to prepare hollow fibre membranes and is based on the phase inversion method (Khayet and García-Payo 2009).

A schematic drawing illustrating the preparation of hollow fibre membranes is displayed in Fig. 2.5. The polymer solution is prepared and stored in a thermostated tank. Then, the solution is pumped and extruded through a tube-in-orifice spinneret; the polymer solution (being filtered before it) enters the spinneret. The viscosity of the polymer solution should be high (more than 100 poise). The bore injection liquid (nonsolvent liquid or gas) is also delivered or passed through the inner tube of the spinneret. The primary function (goal) of the bore liquid is to keep the fibre open and to assist in controlling the interior surface morphology of the hollow fibre through phase inversion.

After a short residence time in air or atmosphere, the fibre is immersed in a coagulation bath where precipitation appears outside the liquid filament due to solvent evaporation. After immediate coagulation, asymmetric hollow fibre are formed with density gradient along the radial direction (Machado et al. 1999). The fibres are then rinsed and cut with the desired length and collected upon a godet. Cutting the fibre is favourable in the hollow fibre process to assist in promoting the flow of bore liquid inside the hollow. The main parameters in the spinning technique are (Mulder 1997):

- (a) The extrusion rate of the polymer solution,
- (b) The bore fluid rate,
- (c) The tearing rate,

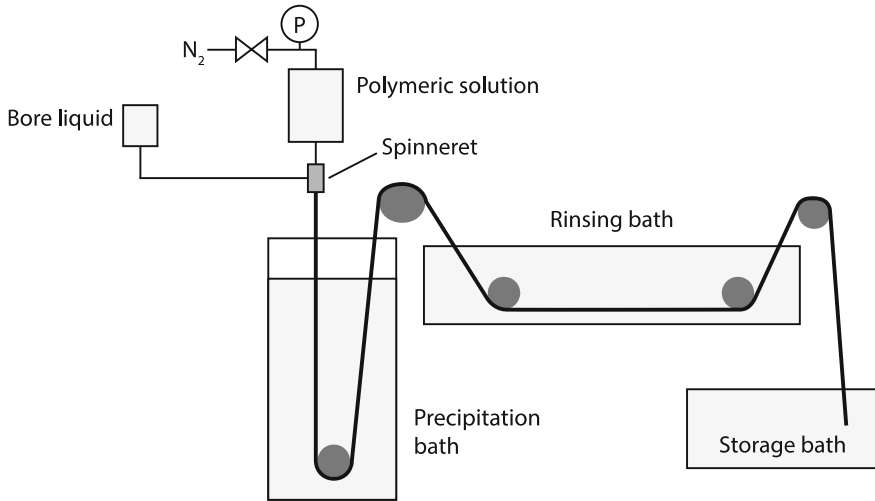


Fig. 2.5 Hollow fibre spinning apparatus. Adapted from Machado et al. (1999), Mulder (1997)

- (d) The residence time in the air gap (between spinneret and coagulation bath), and
 (e) The dimensions of the spinneret.

These parameters strongly interact with the membrane forming parameters such as the composition of the polymer solution, the composition of the coagulation bath and its temperature.

In summary, the configurations of flat sheet and hollow fibre membrane can be used as membrane bioreactors (MBRs) for applications of wastewater treatment, and both have their advantages and disadvantages.

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