

ORGANIC-INORGANIC HYBRID MEMBRANES IN SEPARATION PROCESSES: A 10-YEAR REVIEW

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Abstract - In relation to some inorganic membranes, polymeric membranes have relatively low separation performance. However, the processing flexibility and low cost of polymers still make them highly attractive for many industrial separation applications. Polymer-inorganic hybrid membranes constitute an emerging research field and have been recently developed to improve the separation properties of polymer membranes because they possess properties of both organic and inorganic membranes such as good hydrophilicity, selectivity, permeability, mechanical strength, and thermal and chemical stability. The structures and processing of polymer-inorganic nanocomposite hybrid membranes, as well as their use in the fields of ultrafiltration, nanofiltration, pervaporation, gas separation and separation mechanism are reviewed.

Keywords: Gas separation; Nanocomposite membranes; Nanofiltration; Pervaporation; Transport mechanism; Ultrafiltration.

INTRODUCTION

Every part of a chemical process involves at least one separation or purification stage to facilitate removal and recovery of the required products (Ahuja, 2003a). In recent years, membrane separation processes have developed from laboratory devices to industrial processes with considerable technical and commercial impact (Arthanareeswaran and Sriyamuna, 2009). The main advantages of membrane technology as compared with other unit operations in (bio)chemical engineering are related to the unique separation principle, i.e., the transport selectivity of the membrane. In many cases, membrane processes are faster, more efficient and more economical than conventional separation techniques. Furthermore, they do not require additives, and can be performed isothermally and at very competitive energy consumption levels. Finally, both upscaling and downscaling of membrane processes, as well as

their integration into other separation or reaction processes are easy (Ulbricht, 2004).

In the last three decades, significant improvements in the performance of polymeric membranes for ultrafiltration, nanofiltration, pervaporation, gas separation, and fuel cells have been made (Malekpour *et al.*, 2011; Yi *et al.*, 2010; Ferraz *et al.*, 2007; Mehta and Zydney, 2005; Nyström *et al.*, 1995; Pagliero *et al.*, 1993; Vittadello *et al.*, 2003; Thayumanasundaram *et al.*, 2010), and our understanding of the relationships between the structure, permeability and selectivity of polymeric membranes has been greatly advanced (Geise *et al.*, 2011; Dal-Cin *et al.*, 2008; Cong *et al.*, 2007). Polymeric membrane materials such as poly(trimethylsilyl propyne) (PTMSP), poly(amide imide) (PAI), polyphosphazene (PPN), Poly(dimethylsiloxane) (PDMS), cross-linked polyethylene glycol (PEG) and polyoctylmethylsiloxane (POMS) have been continuously studied (Ozdemir *et al.*, 2006). There are some applications of polymeric membranes in

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industry. For example, commercial pervaporation systems for dehydration of alcohol were introduced in Germany by GFT (a small engineering company) in the 1980s (Baker, 2004). A plant separating air into its constituent gases and producing pure nitrogen at nearly 24 t h^{-1} in Belgium by Praxair Co. began operation in 1996 (Maier, 1998). Since the development of ultrafiltration as a viable industrial process in the 1960s, there have been literally thousands of different ultrafiltration membranes sold commercially. In 1998 there were more than 90 companies providing membranes and/or modular systems for ultrafiltration and microfiltration (Yi *et al.*, 2010). Fuel cells have been known to science since 1839. Proton exchange membrane fuel cells (PEMFCs) were first invented at General Electric in 1959. Although PEMFCs were tested as part of the NASA Gemini program in preparation for lunar missions, ultimately alkaline fuel cells replaced PEMFCs on the Apollo missions (Sandstede *et al.*, 2003). However, these membranes suffered from a lack of durability and mechanical strength. The first significant step in membrane (for fuel cell) research and development occurred in 1966 with DupontTM's production of Nafion® (type of perfluorinated ionomer). Nafion® exhibited significantly improved properties, including doubling the specific conductivity and a four-fold increase in the lifetime (Smitha *et al.*, 2005). Low operational cost, relatively small footprint, and compliance with environmental regulations are the major benefits of polymeric membranes. Organic systems are less chemical and temperature stable than inorganic membranes, but are more versatile in providing different porous structures (Ng *et al.*, 2010; Sforça *et al.*, 1999).

The efficiency of polymeric membranes decreases with time due to chemical degradation, fouling, thermal instability, low fluxes and compaction, as well as the occurrence of swelling phenomenon. The use of pure homopolymers for membrane manufacture led to a stagnation of perspectives when exploring membrane applications in new fields like energy and nanofiltration in nonaqueous medium (Nunes, 2008). On the other hand, it is still difficult and expensive to fabricate large inorganic membranes due to their fragile structures (Koros, 2002). It is believed that the addition of nanoparticles may favour the formation of complexes with the polymer and in turn act as a cross-linking center for the polymer by reducing the tendency of the polymer for self-organization. Also, the large surface area of the nanoparticles prevents the polymer chains from recrystallizing and in addition acts as a support matrix for the polymer (Zuo *et al.*, 2009; Cao *et al.*, 2006).

Organic-inorganic polymer hybrids constitute an emerging research field which has opened the possibility of combining characteristics of both inorganic and organic polymeric membranes and may contribute to solve some of the problems connected to each of them. For example, Bottino *et al.* (2001) studied the preparation and characterization of novel organic-inorganic composite membranes formed by fine silica particles uniformly dispersed in a porous matrix of poly(vinylidene fluoride) (PVDF). Membranes were characterized by ultrafiltration experiments. The results indicated that the thermal properties of the PVDF:silica composite membranes were very similar to those of the PVDF membranes while the mechanical resistance was slightly lower. The most relevant and beneficial effect due to the silica lies in the increase of the viscosity of the casting solutions that makes casting operations easier, especially on a non-woven support, thus allowing the preparation of membranes not only with high mechanical properties, but also with better flux and retention. The effect of various inorganic halides added to a casting solution of poly(acrylonitrile) in *N,N*-dimethylformamide to improve the performance of ultrafiltration membranes was examined by Shinde *et al.* (1999). The addition of di- and trivalent salts resulted in membranes with an average pore size similar to the membrane prepared without any additive. Some polymer-inorganic hybrid membranes show much higher gas permeabilities but similar or even improved gas selectivity compared to the corresponding neat polymer membranes (Kim and Lee, 2001). The effect of zeolite particles incorporated into polymers on the pervaporation properties of membranes was discussed by Boom *et al.* (1998). From the results of the pervaporation experiments it could be concluded that the addition of the hydrophilic zeolite NaX as well as the hydrophobic zeolite silicalite-1 led to an increase in methanol flux and a decrease in toluene flux through the membranes. Mansourpanah *et al.* (2009) studied a procedure for modification of polyethersulfone (PES)/polyimide (PI) nanofiltration membranes, resulting in water flux improvement and minimization of membrane fouling. Hybrid organic-inorganic membrane materials find extensive application in the energy sector (e.g., to devise batteries, fuel cells, supercapacitors, redox flow batteries, etc.). In these systems (e.g., in fuel cells) the membrane separates two compartments fed with different reactants. The membrane is used for ion conduction and allows only the desired species to go from one side to the other, enabling the operation of the device (Di Noto *et al.*, 2011).

This paper does not intend to provide an exhaustive

review of all the polymer-inorganic nanocomposite hybrid membranes developed to date. Recently, Tripathi and Shahi (2011) provided a review of the latest developments in organic-inorganic nanocomposite membranes for application in the energy sector (fuel cells). In the present work, we review the structures and processing of polymer-inorganic nanocomposite hybrid membranes, as well as their use in the fields of ultrafiltration, nanofiltration, pervaporation, gas separation and the separation mechanisms.

CLASSIFICATION OF POLYMER-INORGANIC NANOCOMPOSITE MEMBRANES

The “nanocomposites” are materials comprising a dispersion of nanosized particles in a matrix, where this can be a single polymer or a polymer blend. The definition of nanoparticles differs depending upon the materials, fields and applications concerned. In the narrower sense, they are regarded as the particles smaller than 10–20 nm, where the physical properties of the solid materials themselves can drastically change. On the other hand, the particles in the range from 1 nm to 1 μm may also be called nanoparticles (Hosokawa *et al.*, 2007). The nanostructure, the degree of organization and the properties that can be obtained with nanocomposite materials certainly depend on the chemical nature of their components, but they also rely on the synergy between them. As a consequence, the nature of the interface or the nature of the links and interactions exchanged by the organic and inorganic components have been used to categorize these hybrids (Sanchez and Ribot, 1994). The preparations and structures of polymer-inorganic nanocomposite membranes, their applicability to gas separation and the separation mechanisms have been reviewed by Cong *et al.* (2007) and Guizard *et al.* (2001). They divided the polymeric membranes in two types according to their structure: type (I), polymer and inorganic phases connected by van der Waals force or hydrogen bonds (Figure 1) and type (II), polymer and inorganic phases connected by covalent bonds (Figure 2).

According to Sanchez and Ribot (1994), type (I) corresponds to all the systems where no covalent or ionic-covalent bonds are present between the organic and inorganic components. In such materials, the various components only undergo weak interactions such as hydrogen bonding, van der Waals contacts, π - π interactions or electrostatic forces. On the contrary, in type (II) materials, at least a fraction of the organic and inorganic components are linked

through strong chemical bonds, such as ionic-covalent or Lewis acid-base bonds. Thus, a key point for the design of new hybrids is the tuning of the nature, the extent and the accessibility of the inner interfaces (Sanchez *et al.*, 2003).

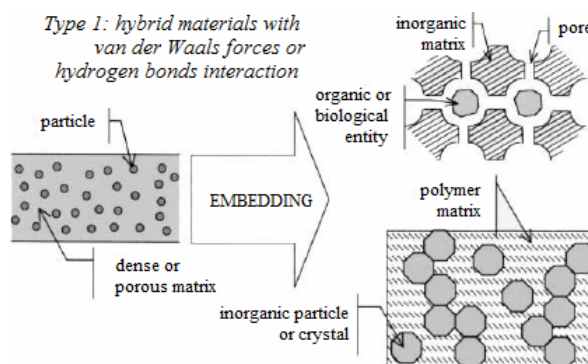


Figure 1: Composite hybrid materials (type I) made of organic or inorganic species embedded in an inorganic or organic matrix (Guizard *et al.*, 2001). (Reproduced with permission from Elsevier Co.)

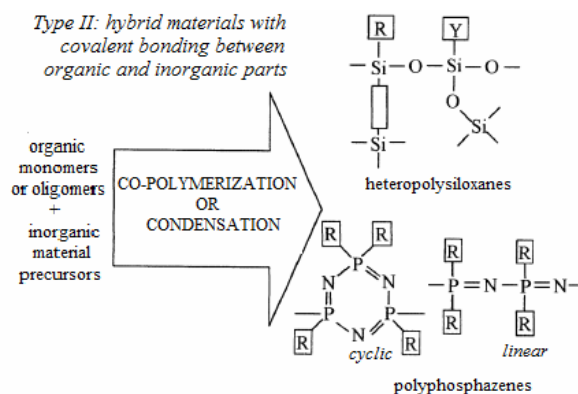


Figure 2: Hybrid materials (type II) based on organic-inorganic polymers (Guizard *et al.*, 2001). (Reproduced with permission from Elsevier Co.)

Because of the differences between the polymer and inorganic phase properties and the strong aggregation tendency of the nanofillers, fabricating an ideal nanocomposite membrane (mixed matrix membrane) (Figure 3) is very difficult (Aroon *et al.*, 2010). Due to the weak polymer-particle adhesion, nanocomposite membranes frequently will show defects at the polymer-particle interface. There are three major categories of interfacial defects (Chung *et al.*, 2007; Moore and Koros, 2005). The first is interfacial voids or sieves-in-a-cage (Figure 4a). The second is a rigidified polymer layer around the particles (Figure 4b), and the third is particle pore blockage.

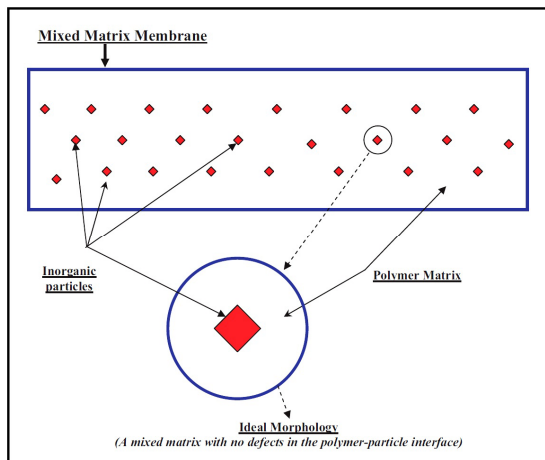


Figure 3: Schematic diagram of an ideal mixed matrix membrane (Aroon *et al.*, 2010). (Reproduced with permission from Elsevier Co.)

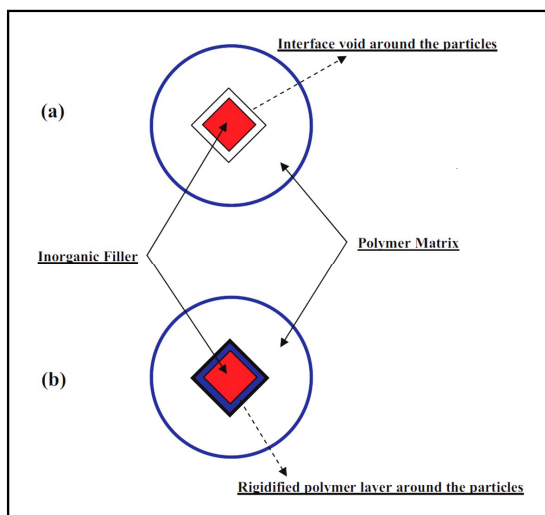


Figure 4: Interfacial void (a) and rigidified polymer layer (b) in the polymer-particle interface (Aroon *et al.*, 2010). (Reproduced with permission from Elsevier Co.)

Rigidified polymer layer formation and interfacial void formation are due to stresses which arise during membrane formation, a result of solvent evaporation or removal. Rigidified polymer layer formation near the particle is related to uniform stress around the particles. In this case, polymer chain mobility in the vicinity of the particle surface is less than in the polymer bulk. If the stress directions are not uniform around the inorganic particles, interfacial voids will be formed at the particle-polymer interface (Aroon *et al.*, 2010; Moore and Koros, 2005). The interfacial defects are hypothesized to form as a result of nucleation of non-solvent and/or a polymer lean phase around the inorganic phase (zeolites) during

the phase separation process. It appears to be necessary that nucleation of solvents and non-solvents at the zeolite surface be restricted. One such approach is via increasing the hydrophobicity of the zeolite surface by capping surface hydroxyls with hydrophobic organic molecules (Husain and Koros, 2007).

Different thermal expansion coefficients of the polymer and particle, repulsive forces between the continuous and dispersed phases, poor polymer-particle adhesion, polymer packing disruption in the vicinity of the inorganic phase and the effects of an elongation stress during fiber spinning are other causes for interfacial void formation (Jiang *et al.*, 2005; Li *et al.*, 2005; Vankelecom *et al.*, 1995). These two interfacial defects may be formed at the porous and impermeable nonporous particle interface when they are added as fillers to the polymer matrix in mixed matrix membranes. But pore blockage is unique to porous fillers. In this condition, particle pores are clogged with a sorbent, solvent, contaminant or minor component in a feed gas or polymer chains, before, during or after membrane fabrication (Aroon *et al.*, 2010; Chung *et al.*, 2007; Clarizia *et al.*, 2004; Mahajan and Koros, 2002). Depending on the pore size of inorganic fillers, one can classify them into total and partial pore blockage. When inorganic filler pores are plugged completely, the gas molecules cannot pass through the particle pores and porous inorganic particles can act as an impermeable filler (Merkel *et al.*, 2003); whereas when pore blockage occurs partially, depending on the gas molecule dimensions and blockage degree, penetrants of interest enter or pass through the pores more slowly than usual (Aroon *et al.*, 2010; Chung *et al.*, 2007; Clarizia *et al.*, 2004).

Aggregation/dispersion behavior control, which is the first process for the preparation of new functional materials incorporating nanoparticles, is very difficult for nanoparticles less than 100 nm in diameter due to surface interactions (Ng *et al.*, 2010). Examples of surface interactions between particles in the liquid phase are shown in Table 1.

The surface interaction can take place when the nanoparticles in polymeric solution fulfill the conditions as stated. Though researchers understand the surface interaction theories, the factors that enhance or further induce the agglomeration remain unclear. This causes difficulty in dispersing the nanoparticles during membrane fabrication. However, Yu *et al.* (2009) suggested that an increment in concentration of nanoparticles could lead to an increase in nanoparticle agglomeration. Besides, Gilbert *et al.* (2009) suggested that ionic strength and pH of the solution also could induce agglomeration between nanoparticles.

Table 1: Examples of surface interaction between particles in the liquid phase (adapted of Schaep *et al.*, 1998). (Reproduced with permission from Elsevier Co.)

Surface interaction	Generation mechanism
van der Waals interaction	Short-ranged electromagnetic force between molecules and/or atoms.
Overlap of electrical double layer	Electrical interaction from the overlap of electrical double layers around particles in solution.
Steric interaction of adsorbed polymer	Short-range interaction due to the overlap of adsorbed polymer layer on particles.
Bridge force	Formation of a bridge of polymer binder and/or surfactant between particles.
Hydration force	Overlap of hydrogen-bonded water molecules on a hydrophilic surface of the particles
Depletion	Negative adsorption of solute and polymer with less affinity for the surface than the solvent

NANOPARTICLE-POLYMER COMPOSITE PROCESSING

Organic–inorganic interfacial defects can dramatically affect overall membrane properties. Therefore, polymer–inorganic nanocomposite membranes cannot be prepared by common methods (Aroon *et al.*, 2010; Cong *et al.*, 2007). There are three general ways to prepare hybrid membranes. The first is the sol–gel process. The second is the phase inversion method, which is also called the *in situ* blending method, and the third is *in situ* or interfacial polymerization.

Sol-Gel Process

The sol–gel technique is the method most applied for the preparation of polymer–inorganic nanocomposite membranes with highly homogeneous and controlled morphology. In this method, organic monomers, oligomers or polymers and inorganic nanoparticle precursors are mixed together in the solution. The inorganic precursors then hydrolyze and condense into well-dispersed nanoparticles in the polymer matrix. The concentrations of organic and inorganic components are easy to control in the solution, the reaction conditions are moderate—usually room temperature and ambient pressure, which allows the formation of inorganic frameworks under mild conditions and the incorporation of minerals into polymers, resulting in an increased chemical, mechanical and thermal stability without obviously decreasing the properties of the polymers (Cong *et al.*, 2007; Cho and Sul, 2001).

For example, Yang and Wang (2006) reported that, by using the sol–gel method, a hybrid ultrafiltration membrane of polysulfone (PS) with titanium

dioxide (TiO₂) as the inorganic phase showed an improvement in porosity and thermal stability. Wu *et al.* (2003a) reported a new inorganic–organic polymer hybrid PEO–[Si(OCH₃)₃]₂ synthesized by coupling N-[3-(trimethoxysilyl)propyl] ethylenediamine (A-1120) to endcapped PEO-400. Based on this hybrid, a series of positively charged membranes were prepared by the sol–gel process. From the coating time control and the concentration of sol, a desired hybrid membrane for nanofiltration can be obtained. The effect of introduction of silica particles prepared by the sol-gel technique on the gas transport properties of a polyimide film was studied by Joly *et al.* (1997). From permeation studies at 3.155 Pa, the composite membrane showed higher permeability (N₂, O₂, CO₂, H₂ and CH₄) coefficients and hydrogen permselectivities than the polyimide one. All these results were explained by taking into account the difference in the imidization degree of the two membranes and the morphological changes which may be induced by the silica nodules in the organic/inorganic interphases. Nanocomposite membranes for gas separations are traditionally comprised of zeolites dispersed in a polymer matrix in order to improve penetrant permeability and selectivity. Zeolites have a variety of drawbacks for this application – chiefly, a limited number of possible zeolite structures – that limit their potential for use in nanocomposites. Metal organic frameworks (MOFs), a new class of microporous materials, are an attractive alternative to the use of zeolites in nanocomposite membranes. The main advantage of MOFs over well-known nanoporous materials is the ability to tune their physical and chemical properties during synthesis by changing the combination of metals and organic linkers. Rational combination of different metal ions and organic

linkers in the synthesis of MOFs results in materials with various pore sizes and connectivities, offering theoretically an infinite number of possible structures (Banerjee *et al.*, 2009). Adams *et al.* (2010) reported a metal organic framework of copper and terephthalic acid (CuTPA) that was synthesized, characterized, and used to make nanocomposite membranes. The particles were dispersed in poly(vinyl acetate) (PVAc). PVAc is a low T_g polymer that has been shown to create defect-free zeolite-polymer nanocomposite membranes and has low gas permeabilities that do not obscure the contribution of the dispersed phase to overall nanocomposite membrane transport (Moore and Koros, 2004; Zimmerman *et al.*, 1997). Pure helium, carbon dioxide, oxygen, nitrogen, and methane permeation experiments were performed and significant permeability and the desired penetrant selectivity enhancements were achieved. Xie *et al.* (2011) prepared polymer-inorganic nanocomposite membranes by crosslinking poly(vinyl alcohol) (PVA), maleic acid (MA) and silica via an aqueous sol-gel route. Membrane characterisation results revealed that silica nanoparticles (< 10 nm) significantly reduced swelling of the membrane. Pervaporation under various operating conditions was carried out to evaluate the separation performance of aqueous salt solutions through the hybrid PVA/MA/silica membrane. Under all operating conditions, salt rejection remained high (up to 99.9%), indicating that the salt rejection performance of the hybrid PVA/MA/silica membrane was independent of the operating conditions due to the non-volatile nature of NaCl. A new series of negatively charged inorganic-organic hybrid membranes was prepared by the sol-gel and oxidation processes of 3-(mercaptopropyl) trimethoxysilane (MPTS) (Wu *et al.*, 2003b). Due to the formation of an inorganic Si-O-Si network during the sol-gel process, the membranes can endure a temperature as high as ~ 250 °C, and thus showed an extraordinary thermal stability compared with a polymeric membrane. Park *et al.* (2008) prepared organic/inorganic composite membranes used two different polymers. BPO₄ particles were introduced into polymers via an *in situ* sol-gel process. Pre-sulfonated poly(arylether ketone) (SPAEK-6F) copolymer and post-sulfonated poly(ether ether ketone) (SPEEK) were used to prepare composite membranes as matrix. Cross-sectional SEM (Figure 5) images for the SPAEK-6F/BPO₄ and SPEEK composite membranes showed that BPO₄ particles were homogeneously introduced into both polymer matrices. The difference in chemical structure between SPAEK-6F and SPEEK gave rise to a more well-separated hydrophilic/hydrophobic nanophase in the SPAEK-6F membranes.

As a result, during the *in situ* sol-gel reaction taking place in the SPEEK or SPAEK-6F polymer solutions, the BPO₄ sol-type particulates are better dispersed in the SPAEK-6F than in the SPEEK polymer solution.

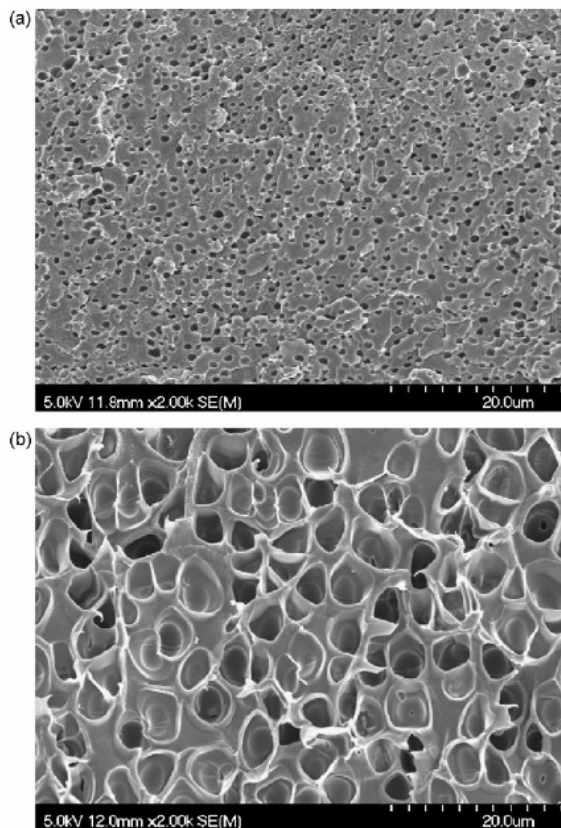


Figure 5: SEM images of cross-sections of composite membranes: (a) SPAEK-6F-40 and (b) SPEEK 6h. (Park *et al.*, 2008). (Reproduced with permission from Elsevier Co.)

Phase Inversion Method

The phase inversion process is one of the most common methods for the preparation of polymeric membranes. The casting solution is cast as a thin film and immersed into a non-solvent coagulation bath. Due to the solvent and non-solvent exchange, phase separation of the casting solution is induced to form a polymer rich phase and polymer-lean phase, and the membrane is thereby obtained (Dong *et al.*, 2012).

For example, Yan *et al.* (2005) reported a study on composite ultrafiltration membranes based on poly(vinylidene fluoride) PVDF and alumina (Al₂O₃) materials by the phase inversion method and investigated characteristics like the membrane hydrophilicity,

porosity, protein retention and surface morphologies. The permeation flux increase of the membrane was attributed to a surface hydrophilicity increase due to the added hydrophilic inorganic nano-sized Al_2O_3 particles. Ghaemi *et al.* (2011) reported a study of nanocomposite membranes containing polyethersulfone (PES) and organically modified montmorillonite (OMMT). The membranes were prepared by a combination of solution dispersion and wet-phase inversion methods. The effect of OMMT addition on the properties and performance of fabricated nanofiltration membranes was investigated. It was observed that the addition of OMMT improved the mechanical properties and thermal stability of the membranes. Moreover, the pure water flux, permeation and rejection of nitrophenols were significantly improved. Zhu *et al.* (2012) prepared hybrid composite membranes by incorporating nano- TiO_2 into regenerated cellulose (RC). The membranes were tested for their ability to separate caprolactam-water mixtures by pervaporation. Among all the prepared membranes, a RC- TiO_2 inorganic-polymer hybrid membrane containing 5 wt.% TiO_2 exhibited good pervaporation performance with a flux of $1787.3 \text{ g m}^{-2} \text{ h}^{-1}$ and a separation factor of 55091.7 at 328 K for 50 wt.% caprolactam. Ahn *et al.* (2008) reported a study on polysulfone (PSF)/silica (SiO_2)

nanocomposite membranes for gas separation prepared by using the phase inversion method. They found that addition of SiO_2 resulted in better thermal stability and significant enhancement of the gas permeability of polysulfone. The permeability, diffusion and solubility coefficients of O_2 and N_2 in PSF in this study were very similar to those reported in the literature, as shown in Table 2. Table 3 shows the permeability, diffusion and solubility coefficients of CO_2 and CH_4 and pure-gas selectivities in PSF at 35 °C.

In Situ/Interfacial Polymerization

In this method, the nanoparticles are well mixed with organic monomers, and then the monomers are polymerized. There are often some functional groups such as hydroxyl, or carboxyl on the surface of the inorganic particles, which can generate initiating radicals, cations or anions under high-energy radiation, plasma or other circumstances to initiate the polymerization of the monomers on their surface (Cong *et al.*, 2007). A large number of research groups have directed their work to the interfacial polymerization method, especially since it is closely linked to production of reverse osmosis membranes. The polymerization of polyamide is most common in these researches.

Table 2: Permeability, diffusion and solubility coefficients of O_2 and N_2 and selectivities in polysulfone at 35 °C (adapted of Ahn *et al.*, 2008). (Reproduced with permission from Elsevier Co.)

P ($\times 10^{-10} \text{ cm}^3 \text{ (STP) cm} / \text{cm}^2 \text{ s cm Hg}$), barrer)		D ($\times 10^{-8} \text{ cm}^2 / \text{s}$)		S ($\text{cm}^3 \text{ (STP) / cm}^3 \text{ atm}$)		$P_{\text{O}_2/\text{N}_2}$	$D_{\text{O}_2/\text{N}_2}$	$S_{\text{O}_2/\text{N}_2}$	Δp (atm)	Reference
O_2	N_2	O_2	N_2	O_2	N_2					
1.29	0.22	3.4	0.85	0.29 ^a	0.19 ^a	5.7	4.0	1.5	10	Ghosal <i>et al.</i> , 1996
1.4	0.25	4.4 ^b	1.22	0.24	0.15 ^a	5.6	3.6	1.6	5	McHattie <i>et al.</i> , 1991
1.4	0.24	4.5 ^b	1.24	0.23	0.15	5.6	3.4	1.7	4.4	Present study

^a S (sorption coefficient) was measured using a transducer barometric device.

^b D (diffusion coefficient) was estimated from permeation time-lag.

Table 3: Permeability, diffusion and solubility coefficients of CO_2 and CH_4 and selectivities in polysulfone at 35 °C (adapted of Ahn *et al.*, 2008). (Reproduced with permission from Elsevier Co.)

P ($\times 10^{-10} \text{ cm}^3 \text{ (STP) cm} / \text{cm}^2 \text{ s cm Hg}$), barrer)		D ($\times 10^{-8} \text{ cm}^2 / \text{s}$)		S ($\text{cm}^3 \text{ (STP) / cm}^3 \text{ atm}$)		$P_{\text{CO}_2/\text{CH}_4}$	$D_{\text{CO}_2/\text{CH}_4}$	$S_{\text{CO}_2/\text{CH}_4}$	Δp (atm)	Reference
CO_2	CH_4	CO_2	CH_4	CO_2	CH_4					
5.5	0.24	2.0	0.35	2.08 ^a	0.67 ^a	23	7.4	3.1	10	Ghosal <i>et al.</i> , 1996
5.6	0.25	2.0	0.34	2.1 ^a	0.56 ^a	22	5.9	3.7	10	McHattie <i>et al.</i> , 1991
6.3	0.22	1.2 ^b	0.27	4.0	0.6	29	4.5	6.5	4.4	Present study

^a S (sorption coefficient) was measured using a transducer barometric device.

^b D (diffusion coefficient) was estimated from permeation time-lag.

For instance, the oxygen permselectivity of a poly[1-trimethylsilyl-1-propyne) (PTMSP) membrane was drastically improved by *in situ* plasma polymerization of fluorine-containing monomers (Lin *et al.*, 1994). Lee *et al.* (2008) reported the fabrication of nanocomposite nanofiltration membranes of polyamide (PA)/TiO₂ by using *in situ* interfacial polymerization. Kong *et al.* (2011) reported the synthesis of inorganic-polyamide nanocomposite membranes on a polysulfone ultrafiltration support via metal-alkoxide-assisted interfacial polymerization. Jadav & Singh (2009) prepared nanocomposite membranes of polyamide and silica nanoparticles by using interfacial polymerization. It was observed that the nanoparticle silica loading significantly modified the polyamide network structure, and hence the pore structure and transport properties. In addition, the nanocomposite membranes exhibited superior thermal stability relative to the pure polyamide membranes. The improvement in thermal stability by the introduction of inorganic silica into the organic polymer was evident from the increase in the glass transition temperatures (*T_g*) of the composite samples measured by differential scanning calorimetry (Figure 6). The *T_g* of the neat polymer was 237 °C and increased to 250 °C for the sample containing a lower amount of silica ~1 wt.%, and to a higher value of 300 °C for the samples of higher silica content ~10 wt.%.

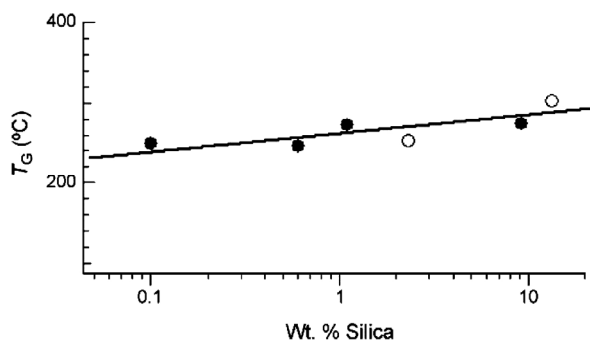


Figure 6: Plot of the glass transition temperature against silica content of the samples; filled and unfilled markers are ‘EX series’ (sample series made from polyamide and LUDOX silica) and ‘IN series’ (sample series made from polyamide and tetraethyl orthosilicate silica) samples, respectively (Jadav and Singh, 2009). (Reproduced with permission from Elsevier Co.)

The *in situ* polymerization only works with suitable monomers, since the intercalation of polymer chains has a quite slow kinetics originating

from diffusion phenomena. For the *in situ* polymerization, one can take advantage of the oxidizing properties of some of the host lattices to induce the polymerization of suitable monomers (Kickelbick, 2003). The key to in-situ polymerization is appropriate dispersion of the filler in the monomer. This often requires modification of the particle surface because, although dispersion is easier in a liquid than in a viscous melt, the settling process is also more rapid (Ajayan *et al.*, 2003).

TRANSPORT MECHANISMS IN MEMBRANES

In general, two mechanisms are used to describe the transport phenomena through a permeation membrane: pore-flow and solution-diffusion. Figure 7 illustrates these two models.

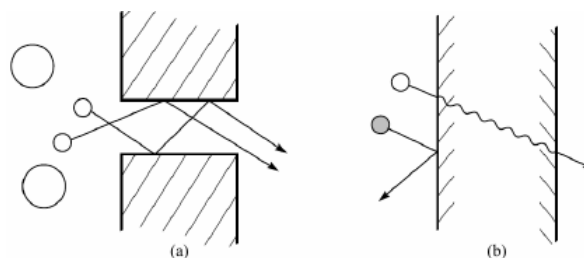


Figure 7: Molecular transport through membranes can be described by: (a) Pore-flow or (b) Solution-diffusion (Baker, 2004). (Reproduced with permission from John Wiley and Sons)

Solution-diffusion is the most generally accepted mechanism of mass transport through non-porous membranes and was first proposed by Graham (Lonsdale, 1982) based on his extensive research on gas permeation through homogeneous membranes. In this model, permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. A separation is achieved between different permeants because of differences in the amount of material that dissolves in the membrane and the rate at which the material diffuses through the membrane. The permeability of gas A, P_A , through a membrane is defined as follows (Matteucci *et al.*, 2007; Matteucci *et al.*, 2008):

$$P_A \equiv \frac{N_A l}{(p_2 - p_1)} \quad (1)$$

where N_A is the steady state gas flux through the membrane; l is the membrane thickness, and p_2 and

p_1 are the upstream (i.e., high) and downstream (i.e., low) partial pressures of gas A, respectively.

If Fick's law is obeyed and the downstream pressure is much lower than the upstream pressure, then permeability can be expressed as follows (Matteucci *et al.*, 2007):

$$P_A = D_A (S_A) \quad (2)$$

where D_A is the effective, concentration-averaged diffusion coefficient of gas A in the membrane. The solubility coefficient of gas A in the polymer, S_A , is given by:

$$S_A \equiv \frac{C}{p_2} \quad (3)$$

where C is the gas concentration in the polymer at the film surface in contact with gas at pressure p_2 .

The ability of a polymer to separate gases A and B is characterized by the ideal selectivity, $\alpha_{A/B}$, which is defined as the ratio of permeabilities (Matteucci *et al.*, 2007):

$$\alpha_{A/B} \equiv \frac{P_A}{P_B} \quad (4)$$

Substituting Eq. (2) into Eq. (4) provides a relationship between the ideal selectivity, the diffusivity selectivity, D_A/D_B , and the solubility selectivity, S_A/S_B :

$$\alpha_{A/B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B} \quad (5)$$

Diffusivity selectivity depends primarily on the relative penetrant sizes and the size-sieving ability of the polymer. Solubility selectivity is controlled primarily by the relative condensability of the penetrants and the relative affinity of the penetrants for the polymer matrix (Matteucci *et al.*, 2008; Freeman and Pinnau, 1999). Both solubility and diffusivity can be influenced by particle type and concentration (Matteucci *et al.*, 2007; Merkel *et al.*, 2003).

Considering a binary mixture along with the polymeric membrane to be a ternary system (for pervaporation), the permeating molecules interact with each other as well as with the membrane (Mandal *et al.*, 2011). The flux of the i^{th} component through the membrane is given by Fick's first law (Pinho, 1990; Ahuja, 2003b) as:

$$J_a = -\rho_m D_a \left(\frac{dW_{am}}{dl} \right) \quad (6)$$

where J_a is flux of component a; ρ_m is density of the membrane phase; d is the dry membrane, and W_{am} is water in the membrane phase of component a.

The diffusion coefficient is not constant across the membrane. The parameters affecting diffusion coefficient are temperature, concentration of the permeating components in the membrane and their coupling effect (Mandal *et al.*, 2011). Assuming constant temperature, the diffusion coefficients for components a and b can be described as (Mulder and Smolders, 1984):

$$D_a = D_{a0} \exp(A_{aa} W_{am} + A_{ab} W_{bm}) \quad (7)$$

$$D_b = D_{b0} \exp(A_{bb} W_{bm} + A_{ba} W_{am}) \quad (8)$$

where the constants A_{aa} , A_{ab} , A_{ba} , and A_{bb} , take into account the change in penetrant mobility in the swollen polymer and D_{a0} is the limiting diffusion coefficient of the considered component at infinite dilution. A_{ab} is the 'plasticization' exerted by the b^{th} component on the diffusion of a^{th} component.

Substituting Eqs. (7) and (8) in Eq. (6) and integrating it over the membrane thickness with the assumption that the concentrations of the permeating components on the downstream are zero (very low pressure) yields the integrated flux for the a^{th} and b^{th} components (Mandal *et al.*, 2011):

$$J_a = \left(\frac{D_{a0} \rho_m}{A_{aa} - A_{ab} l} \right) \left[\frac{\exp(A_{aa} W_{amf} + A_{ab} W_{bmf})}{-\exp(A_{ab})} \right] \quad (9)$$

$$J_b = \left(\frac{D_{b0} \rho_m}{A_{bb} - A_{ba} l} \right) \left[\frac{\exp(A_{ba} W_{amf} + A_{bb} W_{bmf})}{-\exp(A_{ab})} \right] \quad (10)$$

Plasticizing coefficients A_{aa} and A_{bb} reflect the ability of a penetrant to increase self-diffusion, whereas the plasticizing coefficient A_{ab} reflects the ability of a less soluble penetrant to increase the diffusion of the more soluble water (a). It may be assumed that permeability through self-diffusion is far more effective than coupled diffusion. Accordingly, one may assume that $A_{aa} \gg A_{ab}$ and $A_{bb} \gg A_{ba}$. Considering such assumptions, Eqs. (11) and (12) are thus obtained (Mandal *et al.*, 2011):

$$J_a = \left(\frac{D_{a0} \rho_m}{A_{aa} l} \right) \left[\exp(A_{aa} W_{amf} + A_{ab} W_{bmf}) - 1 \right] \quad (11)$$

$$J_b = \left(\frac{D_{b0} \rho_m}{A_{bb} l} \right) \left[\exp(A_{bb} W_{bmf} + A_{ba} W_{amf}) - 1 \right] \quad (12)$$

From the permeation data, J_a and J_b are obtained and from the sorption data W_{amf} and W_{bmf} can be calculated. Thus by regression of these nonlinear equations (Eqs. (11) and (12)) the diffusion coefficient at different feed concentrations along with the plasticization coefficient can be determined. The objective function is the square root of the sum of the square of the difference of the fluxes divided by the number of data points (i.e., N) (Mandal *et al.*, 2011).

$$\text{Objective function} = \sqrt{\frac{\sum_{a=1}^N (J_{\text{exp}} - J_{\text{cal}})^2}{N}} \leq 0.5 \quad (13)$$

Further, the concentration profile of the a^{th} component in the membrane may be obtained as (Mandal *et al.*, 2011):

$$C_{am}(x) = \left(\frac{\rho_m}{(A_{aa} A_{bb} - A_{ba} A_{ab})} \right) \frac{[A_{bb} B1 - A_{ab} B2]}{[A_{bb} B1 - A_{ab} B2]} \quad (14)$$

where

$$B1 = \ln \left\{ \frac{\exp(A_{aa} W_{amf} + A_{ab} W_{bmf})}{+ [1 - \exp(A_{aa} W_{amf} + A_{ab} W_{bmf})]} \right\} \frac{x}{l} \quad (15)$$

$$B2 = \ln \left\{ \frac{\exp(A_{bb} W_{bmf} + A_{ba} W_{amf})}{+ [1 - \exp(A_{bb} W_{bmf} + A_{ba} W_{amf})]} \right\} \frac{x}{l} \quad (16)$$

The pore-flow model assumes that the solvent and solute concentrations within a membrane are uniform and that the chemical potential gradient across the membrane is expressed only as a pressure gradient (Wijmans and Baker, 1995). Permeants are separated by pressure-driven convective flow through tiny pores. A separation is achieved between different permeants because one of the permeants is excluded (filtered) from some of the pores in the membrane through which other permeants move (Baker, 2004; Wijmans and Baker, 1995; Zydney, 2011). For the pure solvent, the permeate flux is directly proportional to the pressure gradient across the membrane (Baker, 2004; Silva *et al.*, 2010):

$$J = A \nabla P \quad (17)$$

where J is flow permeate of the solvent; A is a constant that depends on the morphological characteristics of the membrane and the solution to be processed, and ∇P is the pressure gradient across the membrane.

Assuming that the transport occurs in one direction:

$$J = A \frac{\Delta P}{\Delta X} \quad (18)$$

where ΔP is the pressure difference between the feed and permeate streams (transmembrane pressure), and ΔX is the thickness of the membrane.

Modeling Gas Transport Properties in Nanocomposite Membranes

The influence of solid fillers dispersed in a polymeric matrix on permeability has been studied extensively in the literature. From the theoretical point of view there is a need for a model that describes the permeability of the composite membrane as a function of the permeabilities of the matrix phase and the filler phase, and the amount of the filler. The models commonly used for predicting the permeability through polymer-inorganic nanocomposite membranes are based on the models of Maxwell and Bruggeman.

Maxwell's model, developed to analyze the electrical conductivity of heterogeneous composites (Maxwell, 1973), is often used to model permeability in polymer-inorganic nanocomposite membranes. According to Barrer *et al.* (1963), for membranes filled with impermeable spherical particles, this model reduces to:

$$P_{\text{eff}} = P_C \left(\frac{1 - \phi}{1 + 0.5\phi} \right) \quad (19)$$

where P_{eff} is the permeability of the nanocomposite polymer membrane; P_C is the permeability of the gas in the pure polymer matrix; and ϕ is the volume fraction of nanofiller nanoparticles.

This model partly explains the gas permeability loss in some nanocomposite membranes, especially in polymer-fullerene membranes (Chung *et al.*, 2003). The effective permeability decreases upon increasing the volume fraction of impermeable nanoparticles and is believed to be the result of the reduction in membrane solubility due to the decrease

in polymer content, and of diffusivity reduction due to the increase of the penetrant diffusion pathway length (Cong *et al.*, 2007). However, in general, the addition of fullerene to polymers decreases permeability more than the loss (14%) predicted by Maxwell's model (Saga *et al.*, 2008; Ong *et al.*, 2006; Polotskaya *et al.*, 2006; Labille *et al.*, 2009). Additionally, non-Maxwellian behavior has been observed in numerous other polymer-inorganic nanocomposite membranes. For example, Suzuki *et al.* (2006) reported a study of hybrid membranes based on polyimide/silica and investigated the gas transport properties. It was found that permeability coefficients of the hybrid membranes increased with increasing silica content. The increased permeability suggested the additional formation of free volume holes that were effective for gas transport upon the incorporation of silica. The effect of introduction of aluminophosphate (ALPO) on the gas transport properties of polyethylene (PE) membranes was studied by Covarrubias and Quijada (2010). ALPO was previously swollen with protonated octadecylamine (ODA) and cetyltrimethylammonium (CTA). The permeability results are summarized in Table 4. Permeability to smaller gas molecules increased (He, H₂), while permeability to larger gas molecules tended to remain constant (CO, N₂, O₂). He *et al.* (2002) prepared nanostructured poly(4-methyl-2-pentyne)/silica hybrid membranes for gas separation. The gas permeability increased simultaneously with increasing filler content (Figure 8). Therefore, the silica-filled hybrid PMP membrane showed completely opposite gas permeation behavior to that predicted by the model of Maxwell.

Table 4: Ideal gas selectivity of ALPO/PE composite membranes (Covarrubias and Quijada, 2010). (Reproduced with permission from Elsevier Co.)

Membrane	Selectivity		
	O ₂ /N ₂	H ₂ /CO ₂	H ₂ /CO
PE	3.3	0.2	1.2
ODA-ALPO (2.5%)/PE-in situ	2.3	1.1	4.0
ODA-ALPO (5.0%)/PE-in situ	3.9	1.1	7.3
ODA-ALPO (10.0%)/PE-in situ	1.7	2.3	2.0
CTA-ALPO (2.5%)/PE-melt	2.0	6.5	8.1
CTA-ALPO (5.0%)/PE-melt	3.6	3.6	9.5
CTA-ALPO (10.0%)/PE-melt	3.5	3.9	7.9
ODA-ALPO (5.0%)/PE-melt	1.3	10.6	3.5
PE (ZN)	3.0	0.2	2.6
CTA-ALPO (5.0%)/ZN-melt	1.1	3.1	17
ODA-ALPO (5%)/ZN-melt	3.0	1.2	6.5

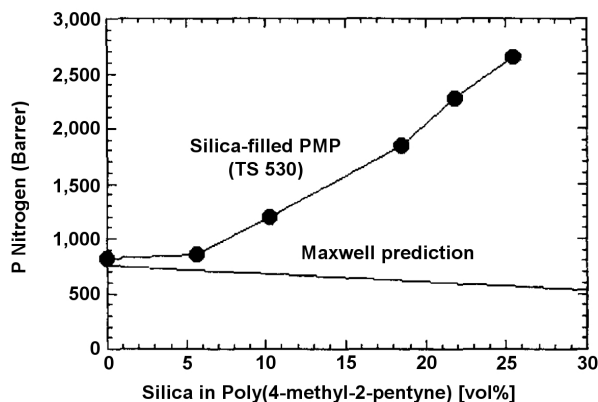


Figure 8: Pure-gas nitrogen permeability of a filled PMP film as a function of filler content. Feed pressure: 50 psig; permeate pressure: 0 psig; temperature: 25 °C (He *et al.*, 2002). (Reproduced with permission from Elsevier Co.)

According to Cong *et al.* (2007) the problem with Maxwell's model lies in its neglect of the interactions between the nanofillers and the polymer chains, and the nanofillers and the penetrants. In most nanocomposite membranes, these interactions are strong, and significantly change the diffusivity and solubility of the penetrants. The Maxwell equation is only applicable to dispersions with low filler content, because of the assumption that the flux pattern around a particle is not disturbed by the presence of other filler particles. The distribution of the filler in the matrix does not have parameters in the Maxwell equation (Bouma *et al.*, 1997).

Bouma *et al.* (1997) recommend the so-called Bruggeman model, which was initially developed for the dielectric constant of particulate composites (Bruggeman, 1935). This model incorporates an integration technique to approximate the effect of adding additional particles to a dilute suspension. The Bruggeman equation for a random dispersion of spherical particles is:

$$\left[\frac{\left(\frac{P_{\text{eff}}}{P_C} \right) - \left(\frac{P_d}{P_C} \right)}{1 - \left(\frac{P_d}{P_C} \right)} \right] \left(\frac{P_{\text{eff}}}{P_C} \right)^{-\frac{1}{3}} = 1 - \phi_d \quad (20)$$

where P_d is the permeability of gas in a dispersed phase; and ϕ_d is the volume fraction of the second phase in the total membrane.

Bouma *et al.* (1997) showed that the Bruggeman and the Maxwell models give fairly identical results

(Figures 9 and 10) up to $\phi_d = 0.20$, after which the presence of nearby particles may affect flow patterns, which unlike the Bruggeman Model, the Maxwell Model does not account for (Vu *et al.*, 2003).

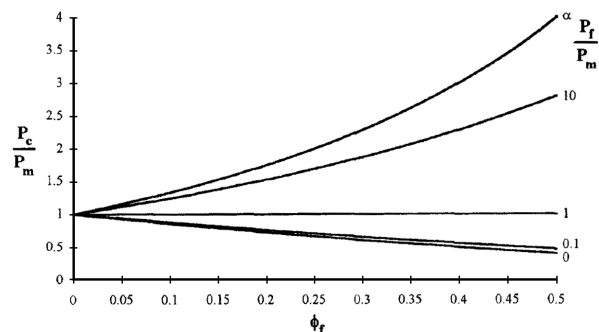


Figure 9: The ratio of composite and matrix permeability versus volume fraction of the filler for various ratios of filler and matrix permeability, ranging from 0 to ∞ . Curves are calculated by applying the Maxwell equation for the permeation through a dispersed system (Bouma *et al.*, 1997). (Reproduced with permission from Elsevier Co.). For the purpose of standardization: $P_c/P_m = P_{eff}/P_c$; $P_f/P_m = P_d/P_c$; $\phi_d = \phi_f$.

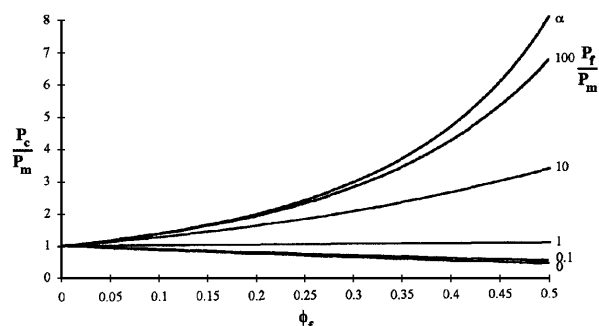


Figure 10: The ratio of composite and matrix permeability versus volume fraction of the filler for various ratios of filler and matrix permeability, ranging from 0 to ∞ . Curves are calculated by applying the Bruggeman equation for the permeation through a dispersed system (Bouma *et al.*, 1997). (Reproduced with permission from Elsevier Co.). For the purpose of standardization: $P_c/P_m = P_{eff}/P_c$; $P_f/P_m = P_d/P_c$; $\phi_d = \phi_f$.

If the hybrid matrix contains an impermeable dispersed phase ($P_d = 0$), this model reduces to Eq. (21). Or if the dispersed phase is much more permeable than the matrix ($P_d > P_c$), this model reduces to Eq. (22).

$$\frac{P_{eff}}{P_c} = (1 - \phi)^2 \quad (21)$$

$$\frac{P_{eff}}{P_c} = \frac{1}{(1 - \phi)^3} \quad (22)$$

The incompatibility of inorganic nanoparticles and the polymer matrix causes void formation; these voids are presumably much more permeable than the polymer matrix. These voids are treated as the dispersed phase in the application of Eq. (22). Hence, this equation is usually compatible with the experimental data up to a good extent and the trend of permeability change can be well anticipated by this model (Shariati *et al.*, 2011).

Modeling Transport Properties in Ultrafiltration and Nanofiltration Membranes

In ultrafiltration and nanofiltration, the transfer mechanism is not yet well known. Thus, each model has been established for specific conditions and, consequently, there is no existing model valid for a wide range of applications. The Hagen-Poiseuille model, which is based on the momentum balance, is the most frequently used to describe flow through porous membranes such as for ultrafiltration and microfiltration. This model (Eq. (23)) takes into account the existence of cylindrical pores, parallel and equal throughout the membrane thickness (Genné *et al.*, 1996; Habert *et al.*, 2006):

$$J = \left(\frac{\epsilon r^2}{8\eta\tau\Delta X} \right) \Delta P \quad (23)$$

where ϵ is the number of pores or porosity; r is the average pore radius; η is the viscosity of the solvent or solution; τ is the tortuosity of the pores; ΔX is the thickness of the membrane, and ΔP is the pressure difference between the feed and permeate streams (transmembrane pressure).

The term $(\epsilon r^2)/(8\eta\tau\Delta X)$ is correlated with the permeability of the membrane (L_p) to solvent or solution, thus:

$$J = L_p \Delta P \quad (24)$$

Eq. (23) shows that the permeate flux is directly proportional to the transmembrane pressure and inversely proportional to the viscosity. The viscosity

is primarily controlled by the solvent type, feed composition, and temperature. Therefore, in the pressure control region, increasing the temperature and pressure, and decreasing the feed concentration can increase the permeate flux (Cui and Muralidhara, 2010).

Several models, all different, are currently available to describe mass transfer through a nanofiltration membrane. These models are based on diffusion, adsorption, ion exchange, ion coupling, concentration polarization or other mechanisms of mass transfer (Garba *et al.*, 1999). For nanofiltration membranes, the most commonly adapted models are those based on the extended Nernst-Planck equation (Eq. (25)). All models based on this equation have been applied to study rejection as a function of flux. At a constant temperature and for dilute solutions, this equation is (Garba *et al.*, 1999):

$$J_i = -p_i \left[\frac{\partial C_i}{\partial x} + \frac{Z_i C_i F}{RT} \frac{\partial \Psi}{\partial x} \right] + (1 - \sigma_i) C_i J_v \quad (25)$$

where J_i is the flux of ion i ; p_i is the permeability of the ion; C_i is the concentration of ion i ; x is a distance variable; Z_i is the number of the ion charge; F is the Faraday; R is the observed salt rejection; T is the absolute temperature; Ψ is the electrostatic potential of the system; σ_i is the coefficient of ion reflection, and J_v is the volumetric flux.

For the tangential filtration module at a constant solvent flow rate, the mobile ion concentration and the electrostatic potential vary essentially in the direction of the flow (x). Thus, partial derivatives (Eq. (26)) become total derivatives, leading to

$$J_i = -p_i \left[\frac{dC_i}{dx} + \frac{Z_i C_i F}{RT} \frac{d\Psi}{dx} \right] + (1 - \sigma_i) C_i J_v \quad (26)$$

Tsuru *et al.* (1999) first proposed such a model for nanofiltration membranes, describing the transport of ions in terms of an effective membrane thickness, porosity ratio, and an effective membrane charge density. The model was successful in describing the rejection of mixed salt solutions. Bowen and Mukhtar (1996) suggested a hybrid model for rejection of a single electrolyte by six nanofiltration membranes. The Donnan-steric-pore model was created by Bowen *et al.* (1997) from a modification of the hybrid model. The model takes into account the hindrance effects for diffusion and convection to allow for the transport of ions/charged solutes taking place within a confined space inside

the membranes. Subsequent studies (Schaep *et al.*, 2001) showed that the model can predict very well the rejection performance of single salt solutions.

CONCLUSIONS

The presence of dispersed inorganic nanoparticles in the polymeric matrix has been useful for the improvement of membrane performance for processes, ranging from gas separation and pervaporation, to nanofiltration and ultrafiltration. Each of these inorganic nanofillers can be incorporated in most of the polymeric materials available in order to produce membranes with specific characteristics, as a result of the synergism in properties between the polymeric materials and nanoparticles. Polymeric membranes modified by adding nanoparticles possess properties of both organic and inorganic membranes such as good hydrophilicity, selectivity, permeability, mechanical strength, and thermal and chemical stability. One of the key limitations in the commercialization of polymer-inorganic nanocomposite membranes is processing. The primary difficulty is proper dispersion of the fillers, because of the difference between the polymer and inorganic phase properties. Without proper dispersion and distribution of the fillers, the high surface area is compromised and the aggregates can act as defects, which limit the properties. Therefore, polymer-inorganic nanocomposite membranes cannot be prepared by common methods. The models of Maxwell and Bruggeman are currently the most widely accepted for predicting gas permeability through polymer-inorganic nanocomposite membranes. The Hagen-Poiseuille model, which is based on a momentum balance, is the most frequently used to describe flow through porous membranes. Each model has been established for specific conditions and, consequently, there is no existing model valid for a wide range of applications. Much research related to preparation and transport mechanisms is still needed to develop better polymer-inorganic nanocomposite hybrid membranes for better application in separation processes.

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