

NANOMEMBRANE MATERIALS BASED ON POLYMER BLENDS

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6.1 INTRODUCTION TO NANOMEMBRANE MATERIALS

The evolution of nanotechnology has led to new opportunities for the use of smaller and more regular structures for porous membranes. A nanomembrane can be seen as the only nano-technological object that can be manipulated without the use of any special equipment. A nanomembrane is a special class of artificial material which is of one the most important developments and a novel and attractive topic in the wide field of nanotechnologies. Nanomembranes are synthetic structures with a thickness less than 100 nm and the aspect of surface-area-volume ratio increases to at least a few orders of magnitude. Nanomembranes continuously fit to nano-objects as a result of their thickness and low-dimensional physics and chemistry. They are related to macroscopic objects due to their large lateral dimensions. The nanomembranes, whose structures are at the same time ultrathin (on the order of nanometers) with large lateral dimensions (of the order of millimeters or even centimeters), and are sufficiently robust to stand freely, without additional support or substrate [1–4]. Studies have shown that a nanomembrane represents a porous membrane with thickness that may be of the order of micrometers, even hundreds of micrometers, but is mesoporous or microporous [5]. Therefore, the existence and dimensions of pores are used as a means of identifying the whole membrane rather than using its thickness, thus the term “nanomembrane” could denote a structure almost a millimeter thick and with a surface which may exceed square decimeters, only because it has nanometer-sized pores. According to Fissell et al. [6], a “nanomembrane” may be any membrane if it consists of a nanostructured material.

Molecular design at the nanometer scale using membranes like polymers offers great potential for high selectivity and high fluxes [7]. Examples of nanopolymer membrane-like materials are cellulose acetate, cellulose nitrate, polyacrylonitrile (PAN), polyvinylchloride, PVC copolymer, aromatic polyamide, aliphatic polyamide, polysulfone, polycarbonate, polypropylene, polytetrafluoroethylene, polyvinylidene difluoride, polydimethylsiloxane (PDMS), etc. [8–11]. Polysulfone membrane possesses excellent mechanical, biological, and chemical stability, as well as having an extensive operating range at temperature ($>80^{\circ}\text{C}$), unfortunately its hydrophobic nature results in low water flux [12]. The hydrophilicity of polysulfone has already been improved in several investigations by chemical modification. It has been observed that the hydrophilicity of polysulfone can be enhanced by introducing charged and polar groups like $-\text{SO}_3\text{H}$ and $-\text{COOH}$ onto polysulfone and these charged as well as hydrophilic polysulfones were used to prepare membranes by blending them with other commercial polymers [13]. The evolution and the sudden expansion of the nanomembrane field have triggered the use of nanotechnologies to accurately control and modify nanomembrane properties at the nanoscale. These novel technologies provide the opportunity to functionalize those already known, but poorly applicable, structures, to design new ones and to tailor both to specific needs. For example, functionalization in synthetic nanomembranes constitutes an important step towards primary extension in different areas of application. These steps include imparting upon the nanomembrane additional important mechanical, chemical, biological, electronic, optical, and magnetic properties, or any of their combinations. The nanomaterials based on polymer blends are attractive, novel nano-building blocks and nanoblends of a support matrix with active nano-dispersed phase. Without functionalization, typically done through nanocompositing, one gets only what blind chance gives, and which may be useful, or more often is not. As in many other situations, a smart design opens many new degrees of freedom [1]. This is obviously achieved by nanocompositing with different kinds of functional building blocks.

This chapter reviews the current state of art polymeric nanomembranes and the concept and development of some mixed-matrix nanomembranes. Methods of controlling the pore shape, porosity, and size of nanoporous polymer materials are also reviewed, together with an analysis of a nano-blend with the nano-phase removed for controlled porosity. Finally, recent progress in mixed-matrix nanomembranes and nanomembrane multi-functionalization of various nanocomposites are discussed.

6.2 CURRENT STATE OF THE ART ON POLYMERIC NANOMEMBRANES

Nanoporous materials are distinguished from bulk nanoporous materials, such as silicon and membranes. Generally, they are materials with holes less than 100 nm in diameter. Bulk nanoporous materials can be classified as natural or synthetic, inorganic or organic, sometimes in combination. The latter can lead to flexible materials being part polymer and part ceramic. Before looking at the current state of art overview and forecasts based on existing information of nanotechnology in the field of polymeric nanomembranes, it is important to look at some features of the two principal microstructural conditions of polymeric material, which are the glassy and rubbery state.

6.2.1 THE POLYMER MATRIX

It has been known for many years that the mechanism of diffusion is very different in rubbery and glassy polymers. This is as a result of the fact that glassy polymers are not in a true state of equilibrium. The difference in mechanisms is reflected in the significant differences observed in the dependence of the diffusion coefficient, as well as the permeability and solubility coefficients, on the penetrant gas pressure or concentration in polymers and on the temperature [14,15]. It is necessary to understand the concept of the glass transition temperature, T_g . As the temperature of a polymer drops below T_g , it behaves in an increasingly brittle manner (the polymer is in glassy state). This is directly related to the restricted chain mobility and the intermolecular forces between the chains do not allow movement other than vibration. As the temperature rises above the T_g , the polymer becomes more rubber-like. Here, the polymers are generally tough and flexible, which is associated with freer chain motion. Rubbery polymers' usually have shorter relaxation times than glassy polymers and respond very rapidly to external stresses. Therefore, a change in temperature causes an instant adjustment to the new equilibrium state. The knowledge of T_g is therefore essential in the selection of materials for various applications. The polymer properties of the two states (glassy and rubbery) can be further modified by the presence of crystalline phases, by stress induced orientations or as a function of cross-link density. They can allow additional constraints on the mobility of the amorphous phase through which diffusion takes place [16–18].

6.2.2 SOLUTION DIFFUSION MECHANISM OF POLYMERIC NANOMEMBRANES

The nanomembranes most commonly used in membrane separation processes are polymeric materials. The separation is based on a dissolution and diffusion mechanism. This mechanism involves molecular-scale interactions of the permeating molecule with the membrane polymer. The mechanism assumes that each molecule is sorbed by the membrane at one interface, transported by diffusion across the membrane through the voids between the polymeric chains (or free volume), and desorbed

at the other interface [19]. This is determined by the affinity of the compound with the polymer the membrane is made of or its ability to dissolve [20]. In a solution-diffusion model, transport only occurs through diffusion. The general approach of a solution-diffusion model is that the permeation of molecules through membranes is controlled by two major parameters: diffusivity coefficient (D) and solubility coefficient (S). Diffusivity is a measure of the mobility of individual molecules passing through the voids between the polymeric chains in a membrane material [19]. If one assumes the diffusion coefficient to be constant, the relationship between the diffusion coefficient, the permeation coefficient, and the solubility coefficient which is the ability of molecules to permeate a membrane is given by Equation (6.1):

$$P = DS \quad (6.1)$$

The permeability coefficient P , defined by the ratio between the flux J of the permeate species and its concentration gradient ΔC over the membrane of thickness d is given as:

$$J = P \frac{\Delta C}{d} \quad (6.2)$$

The ability of a membrane to separate two molecules, for example, A and B , is the ratio of their permeabilities, called the membrane selectivity, α_{AB} [19]:

$$\alpha_{AB} = \frac{P_A}{P_B} \quad (6.3)$$

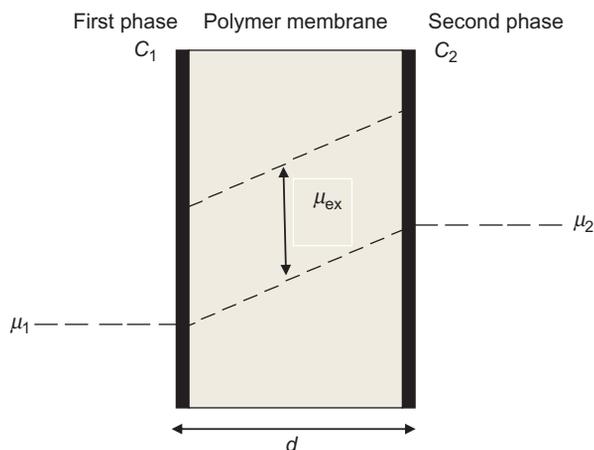
Since P is the product of D and S , Equation (6.3) can be rewritten as:

$$\alpha_{AB} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right) \quad (6.4)$$

D_A/D_B is the ratio of the diffusion coefficients of the two molecules and can be viewed as the mobility or diffusivity selectivity, reflecting the different sizes of the two molecules; S_A/S_B is the ratio of the Henry's law sorption coefficients of the two molecules and can be viewed as the sorption or solubility selectivity of the two molecules. The balance between the solubility selectivity and the diffusivity selectivity determines whether a membrane material is selective for molecule A or molecule B in a feed mixture. Either the diffusivity or the solubility needs to be enhanced to increase membrane selectivity; however, polymers that are more permeable are generally less selective and vice versa [19]. The schematic diagram of polymer membrane is given in Figure 6.1. The driving force behind the transport process which involves sorption, diffusion and permeation is the concentration difference between the two phases [21].

6.2.3 FACTORS CONTRIBUTING TO THE TRANSPORT PROCESS OF POLYMERIC NANOMEMBRANES

The transport behavior of a given penetrate varies from one polymer to the other. Transport properties depend on the free volume within the polymer and on the segmental mobility of the polymer chains [21]. The segmental mobility of polymer chains is affected by the extent of unsaturation, the degree of crystallinity, the degree of cross-linking and the nature of the substituent. The introduction of bulky or polar substituents on a polymer chain influences the transport process. The glass transition temperature of polymers has a great influence on the transport properties. Polymers that exhibit low glass transition

**FIGURE 6.1**

The schematic polymer membrane. Two phases of the membrane were separated with concentrations C_1 and C_2 and chemical potential μ_1 and μ_2 . μ is continuous at the interface and that μ_{ex} which is the excess chemical potential is constant throughout the homogeneous membrane.

temperatures have greater segmental mobility and higher diffusivity. Reports have shown that the polymer molecular weight greatly influences the transport process. As polymer molecular weight increases, the number of chain ends decrease. The chain ends represent a discontinuity and may form sites for permeate molecules to be sorbed into glassy polymers [22]. The transport phenomenon is strongly related to the structure of elastomers [23]. Penetrant mobility in the polymer and the sorption magnitude can be influenced by the chain segmental mobility and the interactions of different elastomers. For an increase in the molecular size from C_8 and C_{16} , the sorption rate and the sorption magnitude decrease [21]. For the same polymer with the same cross-link density, a transport phenomenon depends on the nature of the cross-link [21]. The addition of plasticisers to a polymer leads to an increase in segmental mobility, usually in an increased penetrant transport. The shape and size of a penetrant molecule will influence the rate of transport within the polymeric matrix. Some researchers have reported a decrease in diffusivity with an increase in the size of the penetrant [24–26]. The transport and diffusion in filled polymers depend on the nature of the filler, the degree of adhesion and their compatibility with the polymer matrix. If the inert filler used is compactable with the polymer matrix, then the filler will take up the free volume within the polymer matrix and create a path for the permeating molecules [27].

6.3 CONCEPT OF MIXED-MATRIX NANOMEMBRANES

The development of nanomembranes, where engineered polymer blends are incorporated into the membrane matrix or are deposited on membrane surface, is of great importance. In the development of mixed-matrix nanomembranes the focus is on innovative membrane casting methods, identifying compounds able to keep the polymer blends stabilized in the membrane casting solution, and ensuring compatibility with all membrane components. Nanotechnology is being used to enhance

conventional ceramic and polymeric, water-treatment, membrane materials through various avenues. Among the numerous concepts proposed, the most promising to date include zeolitic and catalytic nanoparticle-coated ceramic membranes, hybrid inorganic-organic nanocomposite membranes, and bio-inspired membranes, such as hybrid protein-polymer biomimetic membranes, aligned nanotube membranes, and isoporous block copolymer membranes [28]. In spite of all the advantages, polymeric nanomembranes cannot overcome the polymer upper-bound limit between permeability and selectivity. Again, some inorganic membranes, such as zeolite and carbon molecular sieve membranes, are known to offer much higher permeability and selectivity than polymeric nanomembranes, but are expensive and difficult for large-scale manufacture. Therefore, it is highly desirable to provide an alternate cost-effective nanomembrane in a position above the trade-off curves between permeability and selectivity [19].

Mixed-matrix membranes (MMMs) are considered as hybrid membranes containing liquid, solid, or both liquid and solid fillers embedded in a polymer matrix [28–45]. They are densely packed polymer membranes with organic or inorganic nanoparticles introduced into their structure. MMMs seek to take advantage of both the low cost and ease of fabrication of organic polymeric membranes, and the mechanical strength and functional properties of inorganic materials [46]. Zimmerman et al. [42] wrote about MMMs as a way to push the limitations of polymeric membranes for gas separation. MMMs have the ability to achieve higher selectivity with greater permeability compared to existing polymer membranes while maintaining their advantages of targeted functionalities, and improved thermal, chemical and mechanical stability. The various material combinations possible with mixed-matrix technology are represented in Figure 6.2 [19]. Improved separation characteristics are achieved by the addition of a dispersed phase to the processable polymer matrix, the net outcome of which should be an improvement in the separation characteristics of the overall membrane (see Figure 6.3). The bulk phase (phase B in Figure 6.3) is typically a polymer or a ceramic support, the dispersed phase (phase A in Figure 6.3) can represent molecular sieves, liquids, or liquid-impregnated sieves.

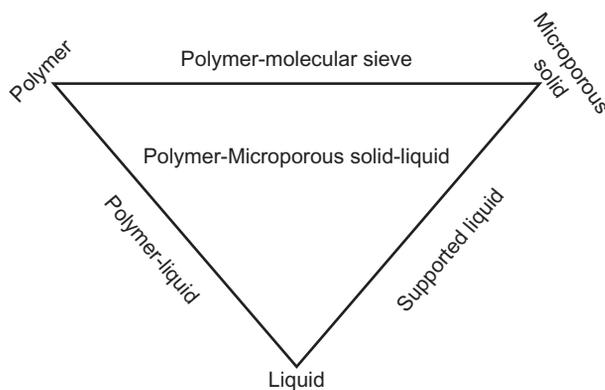
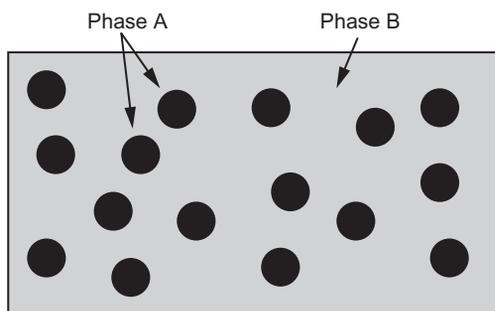


FIGURE 6.2

Materials combination in mixed-matrix polymeric membrane technology.

Adapted from Ref. [19].

**FIGURE 6.3**

Mixed-matrix example: phase A dispersed in phase B matrix.

Adapted from Ref. [19].

MMMs including inorganic molecular sieves, such as zeolites and silicalite, embedded within a polymer matrix are applied in order to provide preferential flow paths for the target species to pass through the membrane [34,47–49]. Theoretically, progressive pathway formation of fast diffusion molecular sieves occurs at a volume fraction of filler material called the “percolation threshold.” At this point, the targeted molecules can traverse the entire membrane cross-section through the filler [42,50]. Above certain high-volume fractions, defects tend to occur at the polymer filler interface limiting selectivity [42].

6.4 DEVELOPMENT OF MIXED-MATRIX NANOMEMBRANES

The term “polymer membranes modified with nanomaterials” defines either modification of the structure or the surface of the membrane. Therefore, the category of MMMs is distinguished. These membranes are produced by introducing nanoparticles into organic polymer structures. Another category is thin-film nanocomposites (TFNs), which is a composite membrane with deposited and cross-linked nanomaterials on their surface [51,52]. In spite of the type and amount of nanoparticles in the modified polymer membranes, their structure is generally asymmetrical and comprises a dense skin layer and a porous supporting layer [53,54]. The differences between the structure of nanomembranes and conventional polymer membranes result from the different size and quantity of pores, and also the thickness of the skin layer formed [51]. MMMs are produced by placing the molecular sieves with a high degree of selectivity dictated by their shape and size (e.g., carbon molecular sieves with pore size allowing for distinguishing penetrants within the polymer matrix) within the membrane matrix. The efficiency of MMMs depends on the type and strength of the physico-chemical interactions between the filler and the membrane polymer [51]. For the nanocomposite TFN membranes, the nanoparticles are deposited on the membrane surface in the process of chemical cross-linking at the interface according to the diagram shown in Figure 6.4 [55].

The hydrophobicity of polymer is a factor that greatly influences the membrane filtration performance. Polymers containing ionized functional groups are hydrophilic. Simultaneously with increasing hydrophilicity, the chemical, mechanical and thermal stability of the polymer decreases [51]. It is related to the hydrating effect of water molecules on the membrane material [56]. There are three main types of MMMs: solid-polymer, liquid-polymer, and solid-liquid-polymer MMMs.

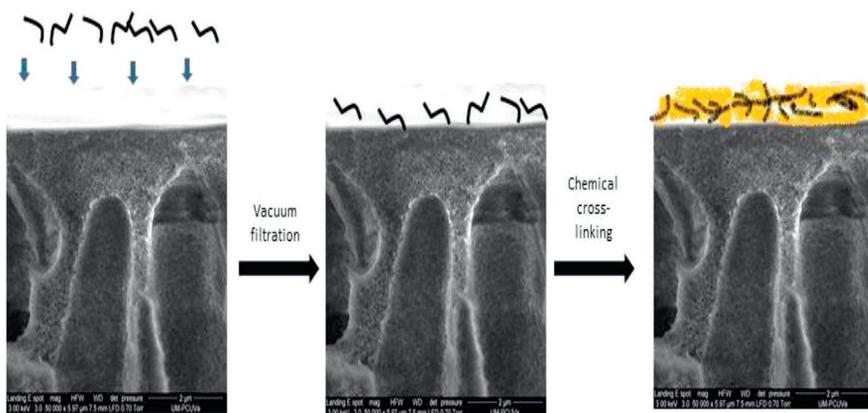


FIGURE 6.4

Formation of nanocomposite membrane: polymer-carbon nanotubes.

Adapted from Ref. [55].

6.4.1 SOLID-POLYMER MIXED-MATRIX NANOMEMBRANES

To date, much of the research conducted on MMMs has concentrated on the combination of a solid molecular sieving phase, such as zeolites or carbon molecular sieves, with a processable bulk polymer matrix. Zeolites are naturally occurring aluminosilicate minerals with highly uniform subnanometer and nanometer scale crystalline structures. Typical zeolite membranes are amorphous silicate, aluminosilicate or aluminophosphate crystalline structures formed via hydrothermal synthesis [57]. Transport of molecules within zeolite crystals is controlled by an adsorption-diffusion mechanism. In zeolites, two types of diffusivities have been identified: transport diffusivities (Fickian diffusivities) and self-diffusivities [58,59]. A few common zeolite materials employed in membranes include MFI-type, sodalite and Linde Type A. Zeolite ZSM-5 (MFI)—the most commonly applied zeolite in membranes is composed of a unit cell with the chemical formula $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192} \sim 16\text{H}_2\text{O}$ ($n \sim 3$) [46]. *In-situ* layer-by-layer crystallization and dry gel conversion in the presence of a template-water vapor are other synthesis methods. The setting of the sieving phase in a solid-polymer mixed-matrix can have a selectivity that is greatly larger than the pure polymer. Thus, the addition of a small volume fraction of sieves to the polymer matrix significantly increases the overall separation efficiency. Though many investigations have been conducted using solid-polymer MMMs, a detailed investigation is required in all the aspect of this new technology [60–62].

The type of morphology that forms at the interfacial region has a direct influence on the separation properties of the membrane. Lai et al. [63] invented a new zeolite membrane which exhibits a columnar cross-sectional morphology and preferred crystallographic orientation comprising a porous substrate, having coated thereon a mesoporous growth-enhancing layer (GEL) and a layer of columnar zeolite crystals on said mesoporous GEL. The mesoporous GEL comprises nanocrystalline or colloidal-sized zeolites, nanocrystalline or colloidal zeolite and metal oxide, or nanocrystalline or colloidal zeolite and colloidal metal, or nanocrystalline or colloidal zeolite, colloidal metal and metal oxide. Their application stems from the belief that the size and shape of the zeolite crystals in the columnar zeolite layer is controlled by properties of the mesoporous GEL. Controlling the morphology, orientation and shape

of the zeolite crystals in the zeolite layer reduces the number of voids between crystals because the crystals pack together such that only grain boundary zones separate them. The GEL layer was believed to nucleate the formation of the dense mat of zeolite crystals grown on the surface of the GEL layer. This dense mat of crystals is closely packed together such that there exists at least one point between adjacent crystals of ≤ 20 Å. As the zeolite layer grows from the interface at the GEL layer, crystal width may increase; however, the individual crystals remain separated at their boundary zones by at least one point of spacing of ≤ 20 . This densely packed mat is the columnar zeolite layer. Void mean a space between adjacent zeolite crystals in the columnar zeolite layer larger than 40 Å. The instant membranes are virtually free of voids in the columnar zeolite layer. Voids are, at most, about 1 V%, preferably less than 0.1 V% of the columnar zeolite layer. Zhou and Nair [64] invented new methods for synthesizing deca-dodecasil 3R (DDR) zeolite nanocrystals (200-2000 nm in size) by using hydrothermal secondary growth (seeded growth). By changing the ratio of silica to water, the synthesis temperature, and the mineralizing agents, the morphology and size of the crystals can be manipulated. Specifically, crystals with morphology of hexagonal plates, octahedral, and diamond-like plates are disclosed. Such crystals can be used as seed coatings for DDR membrane growth on various substrates, and for the fabrication of MMMs, membranes on porous substrates, among other uses. Post-treatment with PDMS solution can be used to seal membrane defects, if any, and the membranes can be used for any small molecule liquid or gas separations, or gas storage, catalysis, and the like. Resulting membranes also have demonstrated acid stability combined with the low $\text{H}_2\text{S}/\text{CH}_4$ and higher CO_2/CH_4 selectivities, indicating a use for selective CO_2 removal from acid gas-loaded natural gas, and possibly the separation of other gas pairs in acidic environments.

Investigations have shown that the interfacial region, which is a transition phase between the continuous polymer and dispersed sieve phases, is of particular importance in successful MMM formation [29,34,35].

For a good sieve-polymer interfacial adhesion, a reduction in free volume is believed to occur near the surface of the sieve, the result is termed matrix rigidification [34]. There is a belief that the layer of rigidified polymer that surrounds the sieves in this morphology displays a lower permeability value than the bulk polymer matrix, resulting in a lower overall membrane permeability [65]. Matrix rigidity should not greatly affect the enhancement in selectivity caused by the sieving phase, except if the rigidified polymer permeability is too low that it effectively starves the zeolites. The change in selectivity with blend composition could be related to phase inversion occurring over a narrow concentration range as is evident from morphology of the blends. Permeation proceeds around the sieve as in the case of the truly plugged sieves, in this latter case. As long as the rigidified polymer permeability is not extremely low, the resulting separation properties should only match the Maxwell model selectivity estimate because permeability will be lower than predicted [19]. The Maxwell model was originally applied to permeation in systems in which the dispersed phase consisted of a low fraction of spherical particles [66].

6.4.1.1 Use of solid-polymer mixed-matrix nanomembranes for gas separation

One of the most significant unit operations applied recently is the membrane-based separation of gaseous mixtures, it has found acceptance in a range of industrial, medical, and laboratory applications. Nanomembranes are filters which are used for separating gases and liquids at a molecular level. They are usually manufactured using organic polymer-based nanocomposite materials with a thickness less than 100 nm [67]. Cross-linkable MMMs are an attractive technology that promises both outstanding

separation properties and swelling resistance for the purification of gas. Air separation (i.e., O_2/N_2), hydrogen recovery (i.e., H_2/CH_4 , H_2/CO , H_2/N_2) and acid gas removal from natural gas (i.e., CO_2/CH_4 , SO_2/CH_4) are common industrial gas separations that utilize membrane technology. MMMs have been developed for gas separation processes in which different types of polymers and rigid filler materials such as zeolite were used for the preparation [68–70]. Here, selectivity is achieved by a combination of permeation rates of the desired gas through the polymer and the filler material [67]. Molecular sieves were initially incorporated by dispersion of zeolites in rubber polymer [71]. Furthermore, the dispersion of zeolite in glassy polymers has been studied [72,73]. Carbon nanotubes have recently been used as dispersed materials in the production of MMMs for gas separation [73–76].

A number of polymers have been embedded with zeolites to form MMMs; however, like Barrer, many researchers note poor adhesion at the solid-polymer interface [19]. The use of silane coupling agents to chemically link polymer to the zeolite particles, membrane formation under high-temperature conditions, and membrane annealing are common tools used to “heal” a poorly adhered, sieve-in-a-cage, and interface [70]. Permeation results for several different zeolites embedded in a polyethersulfone matrix give improvements over neat polymer properties, but only at zeolite loadings above 40 wt% [71,77]. Owing to the nature of MMMs platform technology, numerous types of functional particles can be embedded in the polymeric matrix in order for it to be selected to specifically fit the desired application [67].

6.4.2 LIQUID-POLYMER MMMs

For liquid-polymer MMMs, the physical state of the fillers incorporated into the continuous polymer matrix is liquid such as polyethylene-glycol (PEG) and amines [19]. Existing literature reveals that this new type of membrane is less developed [19]. Liquid-polymer MMMs are a less commonly used mixed-matrix technology, due to the long-term stability encapsulated in the continuous polymer matrix. A new type of MMM has recently been developed in an attempt to deal with the disadvantages of liquid-polymer MMMs. Solids, such as activated carbon impregnated with liquid polymer (e.g., PEG), function as stabilizers of the liquid polymer in the continuous phase. Furthermore, activated carbon increases the MMM performance.

6.4.3 SOLID-LIQUID-POLYMER MMMs

All liquid-polymer MMMs have liquid polymer encapsulated in the continuous polymer matrix. The long-term stability of these membranes for industrial gas separation processes is still a critical issue because of the undesirable leakage of the liquid from the membrane [19]. A new type of MMM known as solid-liquid-polymer MMMs has recently been developed to stabilize the liquid in the polymer membrane [78–82]. Drobek et al. [83] recently prepared poly(vinylidene-fluoride) (PVDF) membranes from a reaction mixture with the following formulation: 16 PVDF: 2 LiCl: 5 H_2O : 77 NMP (wt%). To ensure the complete dissolution of all the reaction components, they slowly added small quantities of the PVDF powder (during 2 h), under vigorous stirring, to the solution of NMP, LiCl and H_2O , initially heated to 80 °C. After complete dissolution of the polymer, the viscous mixture was left without stirring for three additional hours at 80 °C, to ensure the removal of all the entrapped air bubbles. The PVDF membranes were cast by pouring the hot sol on a glass plate and spreading it by a tape casting system with 0.6 mm gap set. The glass plate with the cast

polymer film was subsequently soaked for 2 h into the coagulation bath (H_2O /propan-2-ol 50/50 wt/wt). The as-formed membranes were placed for 3 h in a pure water bath to remove all the residual solvents. Finally, the membranes were dried for 24 h in a ventilated oven at 50 °C. They further prepared MMMs by uniform dispersing MFI zeolite fillers (silicalite-1 (S-1) and Ti-silicalite-1 nano-seeds) in the PVDF solution with loadings varying from 15 to 22 wt%. Zeolite seeds were prepared separately by an MW-assisted hydrothermal method and the composite PVDF-derived membranes were prepared by the non-solvent induced phase separation technique, as in the case of pure PVDF membranes. The mechanical properties of the membranes were reduced by the addition of the filler, although the mechanical resistance of the MMMs was still sufficiently preserved. Experiments of hexane adsorption were carried out in order to evaluate the performance of the adsorbers in volatile organic compounds (VOCs) removal. The as-prepared composite porous membranes revealed high adsorption capacity, confirming their potential as adsorbers for removing VOCs traces from waste air environment.

6.5 A NANO-BLEND WITH THE NANO-PHASE REMOVED FOR CONTROLLED POROSITY

Many efforts have been made in the design and fabrication of controlled organic/inorganic composites with novel properties, which include chemical, optical, electrical, biological, and mechanical properties [84–87]. For these hybrid systems, phase separation occurs naturally based on the fact that they are composed of two materials with totally different chemical characteristics [88,89]. MMMs are fabricated from polymer matrix and inorganic particles for improvement polymeric membrane properties. Dispersed particles in polymeric matrix are categorized in two groups: porous and dense (non-porous) particles [90].

Porosity can be defined as the fraction of the pore volume occupied by pore space; or the volume of the pores divided by the volume of the material. Some porous polymer materials have been shown to be of practical use in the last decades. Porous polymer materials have recently become of immense interest to study arena in the development of new materials, because of their potential for applications in fuel cell membranes, chemical filtration, tissue engineering, adsorbents, catalysis, sensors, separations, electrochemical cells, storage and drug delivery, etc. [91–94].

There are many ways to make nanoporous films, such as by lithography [95,96] or the sol-gel method [97,98]. One other possible approach is to create a two-phase mixture and remove the minority phase through physical or chemical means [99]. Porous polymer films represent a distinct, yet important, subclass of responsive multi-functional materials [100,101]. Thin films with well-controlled nanoscale porosity—most interesting from the point of view of practical applications—are primarily from the multiphase materials through the selective removal of one of the polymeric phases or a sacrificial colloidal component in hybrid films. Some researchers proposed self-assembly methods based on liquid-liquid phase separation in multi-component solutions comprising a stimuli-responsive cross-linkable polymer and a pore-forming component [102–104]. The phase separation occurred during spin-cast deposition of polymeric films. Tokarev et al. [102] used monovalent salt to disrupt a polyelectrolyte complex of two biopolymers (alginate and gelatin), thus triggering their phase separation in spin-cast films. Hydrogen bonding between two water-soluble polymers can be also used to delay phase separation, as was demonstrated for the system composed of alginate and poly(vinyl alcohol) (PVA) [104].

Porous alginate gel films (membranes) were obtained by treatment with an aqueous solution containing calcium ions, which caused an immediate gelation of the alginate phase through the ionic cross-linking mechanism well described by the “egg-box” model [105] and removal of the second pore-forming polymeric component into the solution.

Phase morphologies of immiscible binary homopolymer blends evolve from circular domains of one phase dispersed in the matrix of another through a bicontinuous domain structure to the inverse case of the former [106]. When a blend is deposited in thin films, its morphology is also affected by interactions of the polymers constituting the blend with the film interfaces.

This may lead to the formation of thin wetting layers, whereas most of the material occupies laterally distributed (two-dimensional) domains [106]. The lateral microstructures comprising circular and bicontinuous domains were specifically observed for the aforementioned alginate-PVA blend.

Tokarev et al. [107] reported a novel polymer blend system that yields thin films with unique porous nanoscale morphologies and environmentally responsive properties. The blend consists of sodium alginate and amine end-terminated PEG, which passed through phase separation during film deposition. The blend films can be readily converted into highly porous membranes using facile treatment with a solution containing divalent ions. The resulting membranes are primarily comprised of alginate hydrogel, whereas the PEG phase is removed from the films during exposure to the saline solution, yielding nanometer-sized pores. The alginate gel phase formed a three-dimensional nanostructure which they described as a filament or fibrous network. Because of ionizable carboxyl groups, the hydrogel membranes demonstrated responsive behavior, in particular a drastic change in their porosity between a highly porous state and a state with completely closed pores in response to changes in the solution pH. The pore-size tunability can be explored in multiple applications where the regulation of material's permeability is needed.

6.6 METHODS OF CONTROLLING THE PORE SHAPE, POROSITY AND SIZE OF NANOPOROUS POLYMER MATERIALS

Creating new polymer materials with desirable properties by blending different polymers is a common practice. In a two-phase polymer blend, two types of morphologies can be encountered: disperse/matrix and co-continuous morphology. In general, at low concentration of one phase, the morphology is the former; increasing the concentration of the minor phase leads to the latter; at higher concentrations phase inversion leads once again to disperse/matrix morphology [108]. The pore size of nanomembrane materials based on polymer blends can be defined by the phase size of one of the phases in the blend and hence composition, interfacial tension, viscosity ratio and other parameters influencing phase morphology can be used to control porosity. Though, the preparation of the nanoporous structure is important, the important issues are the control of the pore size, distribution and connectivity of the pores within the material. There are many factors that would influence these factors, such as polymer blend composition, molecular weight of the blend components, thermal history, and processing conditions.

In order to study the effects of these on the final pore structures, a careful characterization of the pores is necessary [99]. Previous techniques to control the size of nanoporous membranes involve coating pores with polymers [109] or metal [110]. While polymer coatings are relatively easy to

deposit, they are unable to withstand high temperatures and harsh chemical environments. In the past decades, different methods have been developed to control the porosity, pore shape and size of nanoporous polymer materials, including hard/soft template, self-assembly, and high internal phase emulsion (HIPE) polymerization [111]. Amongst the characterization methods that can be used for this purpose are electro-spinning, gas sorption, mercury injection, permeation test, and optical methods (direct observation).

6.6.1 ELECTRO-SPINNING

The versatility of the electro-spinning process allows for controlling not only the fiber size, morphology and macroscopic assembly, but also, and more importantly, tailoring of the optical properties of the fiber. Electro-spinning has turned out to be a better choice because of its simplicity, economy, scaling capability [112] and control over the nanomembranes morphology [113].

Khalil and Hashaiekh [114] found that when using different proportions of NiAc in the solution containing PVA as a polymeric component, the diameter and roughness of NiO nanofibers (NFs) can be easily controlled and an optimum proportion of NiAc is mandatory for obtaining smooth and continuous fibers. The diameter of these NFs can be further reduced by increasing the electro-spinning voltage. They found that the average NF diameter for the four solutions as a function of electro-spinning voltage and we found that the diameter of individual NFs can be significantly reduced by increasing the electro-spinning voltage without affecting the NF morphology (see Figure 6.5). Aliyev et al. [115] developed and constructed the pulse electro-spinning to produce nano-sized particles, with the ability to control their size. In the pulse electro-spinning setup, unlike the classical setup, high voltage was applied in the form of controlled pulses, which achieves a controlled fiber length.

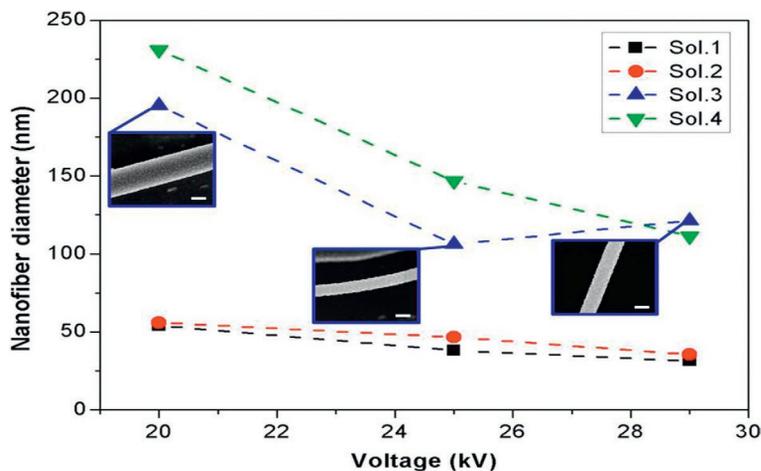


FIGURE 6.5

Variation in the average diameter of NiO NFs as a function of electro-spinning voltage.

Adapted from Ref. [112].

6.6.2 GAS SORPTION

The analysis of gas adsorption/desorption isotherms is widely used for the characterization of porous materials with regard to their surface area, pore size, pore size distribution, and porosity, which is important for optimizing their use in the practical applications of nanomembranes based upon polymer blends. Furthermore, significant progress has been achieved during recent years with regard to the understanding of the adsorption mechanism of fluids in materials with highly ordered pore structures [116,117]. This has led to major improvements in the pore size analysis of nanoporous materials. However, there are still many questions concerning the phase and sorption behavior of fluids in more complex pore systems, such as materials of a heterogeneous nature/differing pore structures, which are of interest for practical applications in catalysis, separation, and adsorption [118].

6.6.3 OPTICAL METHODS

Recently, an increasing amount of investigation has been focused on exploring the production of novel nanoporous materials and polymer blends for their application in the development of nanomembranes. These nanomembranes based on nanoporous materials and polymer blends are highly sensitive due to the large surface-area-volume ratio. The pore size, shape and density of nanomembranes can be varied in a controllable manner depending on the irradiation process parameters. Controlling pore size is critical in the size-dependent separation applications. Pore sizes and the structures of nanomembranes were studied by an optical microscope (OM) during an investigation of polycarbonate nanomembrane production based on alpha particles irradiation [119].

6.6.4 PERMEATION TEST

Permeation testing is a process by which a chemical penetrates through a polymeric material by means of molecular diffusion. This test is directly related to the concentration gradient of the permeate, the material mass diffusivity and the material intrinsic permeability. Farhangi et al. [120] pointed out that for gas separation, the membrane must have small enough porosity and pore size so as to increase the selectivity, and a thinner skin layer so as to improve gas permeation flux. The role of the interface on continuity development for PE/PS systems was investigated [121]. It was shown that the pore sizes in those systems could be controlled from 0.3 to 6.3 μm . It was also demonstrated in another study that the morphology of a 50PE/50PS blend maintains continuity, but coarsened significantly upon quiescent annealing at 200 °C. An annealing time of 75 min resulted in a 25-fold increase of the phase diameter of this blend [122]. Sarazin et al. [123] studied co-continuous poly(L-lactide)/polystyrene immiscible blends for biomedical applications. The microstructure and the region of dual-phase continuity were examined for both binary and compatibilized PLLA/PS blends prepared by melt mixing. It was demonstrated in their studies that highly percolated blends exist from 40% to 75% PS and 40% to 60% PS for the binary and compatibilized blends, respectively. Extraction of the PS phase was found to be a route to generating completely interconnected porosity in poly(L-lactide) materials of highly controlled morphologies (pore size, void volume). Bubble point and gas permeation method was used to measure the pore size and pore size distribution of the membranes prepared by extraction [124]. The “bubble point” is the minimum pressure required to displace the liquid agent from the largest pores. The main test was divided into two subtests. Following the solute permeation test, apparent rejection was a technique that was used to characterize the separation performance of the membrane.

6.7 RECENT PROGRESS IN MIXED-MATRIX NANOMEMBRANES

Recently, MMMs comprising nanoparticle fillers are emerging. These membranes are also called polymer-nanocomposite membranes. Nanocomposite membranes can be considered as a new group of filtration materials comprising MMMs and surface-functionalized membranes. Isodimensional nanoparticles are commonly used as nanocomposite fillers because they provide the highest surface area per unit volume [43].

MMMs are based on the application of nanofillers, which are added in a matrix material. In most cases, the nanofillers are inorganic and embedded in a polymeric or inorganic oxide matrix [125]. These nanofillers feature a larger specific surface area leading to a higher surface-to-mass ratio [126,127].

The applications of nanoparticles for membranes are usually prepared through the sol-gel process, which yields high-purity samples and allows the control of nanoparticle size, composition, and surface chemistry [128,129]. Other formation processes are inert gas condensation, spray pyrolysis, laser pyrolysis, flame spray pyrolysis, pulsed laser ablation, spark discharge generation, ion sputtering, photothermal synthesis, thermal plasma synthesis, flame synthesis, low temperature reactive synthesis, mechanical alloying/milling, mechanochemical synthesis, and electro-deposition [43,128]. Li et al. [130] recently reported the first mixed-matrix composite membrane made of commercially available poly (amide-*b*-ethylene oxide) mixed with the nano-sized zeolitic imidazole framework ZIF-7. The ZIF-7 nanoparticles was synthesized and dispersed in a polymer matrix. This hybrid material was successfully deposited as a thin layer (less than 1 μm) on a porous PAN support. An intermediate gutter layer of PTMSP was applied to serve as a flat and smooth surface for coating to avoid polymer penetration into the porous support. High performance ZIF-7 MMMs for gas separation were manufactured. Excellent compatibility between filler and polymer was observed.

Metal oxide nanoparticles (Al_2O_3 , TiO_2) can help to increase the mechanical and thermal stability as well as permeate flux of polymeric membranes. The incorporation of zeolites improves the hydrophilicity of membranes resulting in raised water permeability. Antimicrobial nanoparticles (nanosilver, CNTs) and (photo) catalytic nanomaterials (bimetallic nanoparticles, TiO_2) are mainly used to increase resistance to fouling [125].

Gehrke et al. [131] recently used a dip-coating process to deposit photocatalytic TiO_2 nanoparticles (P25, Evonik) on a metallic filter material (micro-sieve). The fouling repellent and photocatalytic nano-coatings degraded the water impurities close to the micro-sieve surface before a dense cake layer was formed. This kind of surface activation is, however, restricted to chemically robust materials, excluding polymeric membranes that would be degraded by the induced oxidation process [125].

6.7.1 NANOMEMBRANE MULTI-FUNCTIONALIZATION OF VARIOUS NANOCOMPOSITES

Functionalization of simple nanomembranes is mostly equal to their nanocompositing.

Thus the introduction of two or more phases, each of which contributes to its desirable properties, in order to obtain a super-structure with predesigned multifunctionality. The dimensions of the introduced phases will obviously have to be sufficiently small to fit into such a low-dimensional nanocomposite, which itself has a nano-metric thickness [1]. Multi-functionalization of nanomembranes may, therefore, be viewed as the extreme case of TFN. Apparently, the effective parameters of a composite nanomembrane are expected to be superior to those of each of the separate constituent phases. Apart from the combination and the enhancement of the existing properties of the constituents, completely

novel effects and functions appear in certain situations. A good example is electromagnetic optics of membranes with ordered arrays of pores. Instead of only modifying the transmission and reflection, such structuring introduces the novel effects, even the quite exotic and unexpected ones like negative refractive index or extraordinary optical transmission (super-transmission) [132], none of which have been observed in nature ever before.

The functionalities that can be introduced to nanomembranes are immense. Mechanical properties like elasticity, wear, and tribological (typically lowering of friction) and hardness properties could be enhanced. Electric conductivity may be increased or decreased, magnetic properties imparted, plasmonic behavior introduced or modified. Wettability may be decreased or increased by surface corrugations or patterning. Thermal behavior (e.g., extreme values of thermal conduction, etc.), and chemical activity may be tailored [1]. Optical and electromagnetic properties can be modified, including changes of the effective refractive index in vast range, introduction of antireflection properties, introduction and improvement of photoluminescence, and tailoring of dielectric permittivity and magnetic permeability. Unique structural, electronic, and optical properties have been measured for these nanomembranes, both for flat and curled films [133–135].

Phases in a nanomembrane can be separated along the film thickness (lamination); it can also be distributed within a single stratum which is of granular nanocompositing. For example, a phase diagram for possible band offsets and single-element electronic super lattices created by periodic strain as a function of nano-stressor size, period, and nanomembrane thickness has been calculated [136]. A special case of great importance is the introduction of pores into the nanomembrane. Besides changing the structure and composition, one may impart functionalization by changing the geometry of the nanomembrane, for instance making surface corrugation (sculpturing) [1]. Fabrication of NFs and membranes made of conductive electronic polymers has recently been demonstrated to be useful in the design and construction of nano-electronic devices [137,138].

6.8 SUMMARY

Over the past decade, mixed-matrix nanomembrane has gained research interest from both academia and industries. These research activities are aimed at overcoming the polymer upper-bound limit by including solid, liquid or a combined liquid-solid into the polymer phase. Already mixed-matrix nanomembrane concepts based on polymer blends have led to new modified nanomembranes. The sudden expansion of the mixed-matrix nanomembranes in different fields originates from the possibility of using nanotechnologies to accurately control and modify nanomembrane properties at the nano-level. Nanoscale solute transport of a nanomembrane is controlled by the primary interactions operating in the condensed state of matter: electrostatic, electrodynamic and chemicals. Porosity strongly determines the important physical properties of materials, such as durability, mechanical strength, permeability, and adsorption. The application, concept, design, and testing modifications needed to develop or improve the nanomembranes are identified.

A detailed understanding of the driving force behind the transport process and molecular transport mechanism of transport species through the mixed phase of solid-polymer, liquid-polymer, or solid-liquid-polymer of the mixed-matrix nanomembrane is very important. Factors contributing to the transport process of the modified mixed-matrix nanomembranes based on polymer blends should not be neglected, because the transport behavior of a given penetrant varies from one polymer to another.

Functionalization represents granular nanocompositing of the membrane. Introduction of different phases into a single plane of the film results in a binary, ternary, or higher composite. Functionalization and the general modification of nanomembranes could be considered as an expanding body of knowledge of nanotechnologies. Although related investigations regarding functionalized nanomembranes are still new, they seem to have a bright future and already existing achievements look extremely promising.

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