Chapter 6

Porous Membrane and their Applications

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Abstract

Porous membranes have several uses in separation technology. This chapter basically explored various fabrication routes of different types of porous membranes and their applications in industrial and biomedical fields. The urgent need of a low cost perfect membrane needs to be optimised with good mechanical strength, chemical resistance, and thermal stability. This chapter focuses on producing porous polymeric/ceramic membranes with nano/submicron holes using block copolymer self-assembly, track etching, 3D printing, nanoimprinting, lithography, and electrospinning, etc. Porous polymeric/ceramic membranes are used in separation techniques in various industries, drug administration, bioseparation, and biosensing. The effect of membrane material, pore shape and size towards the membrane performance for various technological challenges are thoroughly discussed.

Keywords

Porous Membranes, Polymeric Membrane, Ceramic Membrane, Separation Techniques, Industrial Application, Biomedical Applications

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1. Introduction

Research progressed on porous membranes is one of the critical importance in the development of science and innovation. Porous membranes have promised tremendous potential in industrial and biomedical applications, because of their primary adaptability, flexible surface science, and bio-compatibility. Recently porous polymers have drawn

tremendous research interest due to its various applications, including gas adsorption/stockpiling, detachment, catalysis, ecological remediation, energy, optoelectronics, and wellbeing. Ongoing years have seen enormous exploration leap forwards in these fields on account of the remarkable pore structures and flexible skeletons of permeable polymers. Although there are various research articles available, explaining characteristics, fabrication and its potential applications in biological and biomedical fields. But most of them have put their interest in a specific technique and its application based on that technique. In this particular chapter, we try to cover all the synthetic procedures available for the preparation of porous membranes out of polymers as well as ceramic materials.

Porous materials consist of a strong framework with characterized openings or pores which have pores of different size from 2 nm to 20 mm [1]. The partition of solutes by permeable membrane (PM) is principally a component of sub-atomic size and layer pore size dispersion [2]. These layers are utilized to segregate colloidal particles or huge subatomic solutes out of solvent. High separation may be acquired when the size of the dissolved or dispersed material (molecules or small particles) are moderately bigger than the pore diameter of the membrane. Utilizing the definition of pore size as embraced by the IUPAC, the PMs are classified based on their pore size. Pore size having 50 nm or more is named macroporous, pore widths somewhere in the range of 2-50 nm are grouped as mesoporous materials. Membrane with normal pore widths somewhere in the range of 0.2-2.0 nm is named microporous. If the pore size is less than 0.2 nm, layers are categorized as nonporous membranes. Based on the membrane architecture, membranes can be categorized as symmetric as the pore diameter does not fluctuate from any cross sectional view. A wide scope of inorganic materials, for example, metals, glasses, ceramics, or natural including various classes of polymers can be utilized to create porous membranes. The material choice also, pore size of the membrane rely upon the application for which it would be utilized.

Since the last two decades, polymer membrane fabrication technique has improved drastically. The first portion of this survey gives a concise summary of various fabrication techniques for polymeric based membranes. These techniques incorporate various methodologies, for example nanoimprinting and track etching based on top-down approaches and block-copolymer self-assembly and electrospinning on bottom-up approaches and the second portion of this survey covers numerous applications.

2. Different fabrication techniques

This section depicts the most commonly used methods for making porous polymeric membranes, including track-drawing, nanoprint lithography (NL), 3D printing, block-copolymer self-assembly and electrospinning.

2.1 Nanoimprint lithography(NL)

Nanoimprint lithography (NL) is the most unique well-known sensitive lithography-based methodology for producing permeable polymeric membranes. This lithography technique became well-known for its tremendous potential for growth because of simplicity, as well as the time effectiveness and low cost. It's a technique where a template is pressed against the opposing layer which is basically distorted on a substrate, i.e. a metallic surface or a silicon wafer. Mould fabrication is the best fundamental factor, since the precision and composition are essential in defining the structure, i.e. engraved polymers. Two of the most widely used nanoimprint lithography techniques are thermal nanoimprinting (TNL) and photo nanoimprinting (PNL) [3]. To create nano and microstructural patterns in a regulated way, photolithography, also known as electron beam lithography (EBL), at nanoscale is often used to make the master mould. EBL, on the other hand, offers permeable anodic aluminium oxide (pAAO) membranes with uniform straight nanochannels that may be used as a format to build nanoscale masters since pAAO films exhibit uniform nanochannels are very easy to manufacture. Nickel (Ni), silicon (Si), and thermoset polymers are used to make master moulds. Because of its flexibility and strength, Ni is the most widely used of these materials. A tiny nanoscale master is created for soft lithography by mixing hard polydimethylsiloxane (hPDMS) with a PDMS mould, since hPDMS has a considerably better resolution than PDMS [4]. Choi and co-workers used a limited adjustable SU-8 stencil membrane to construct a polymeric double scale nanoimprinting mould [5]. Photolithography, from one perspective, included spinning a layer of photoresist (PR) on a slice of device material and then PR exposed to UV light through a mask. Thermal nanoimprinting, on the other hand, included making microscale openings on the equal proportion, mixing a layer of PR and SU-8 layer which is a epoxy based negative layer. Thermal nanoimprinting was used to create a PMMA (polymethyl methacrylate) substrate with nanoscale cavities for the next layer. Ultimately, to get a two-layer micro and nanostructure layer, a SU-8 film was applied to the PMMA substrate. After UV exposure, PUA511RM, an UV curing resin was apportioned against the collected substrate and took off utilising an adaptable PC membrane as a supporting backplane, after an extremely PDMS thin layer was deposited following that siliconization of the hybrid structure to work with the arrival of the last master shape. Lee and coworkers demonstrated the utilisation of delicate lithography to adjust the pattern thickness by warming thermoplastic substrate [6].

2.2 Photo nanoimprint lithography (PLN)

The photo nanoimprinting approach, in contrast to the thermal nanoimprinting method, entails emblazoning the perfect instances on a layer of fluid photoresist and relaxing it by UV irradiation, that causes the oppose to solidify by causing polymer cross-linking. Over the TNL same, the PLN method has a few distinct advantages. It may lead at room temperature at first, which avoids problems caused by thermal development differences between the resist, form and substrate. Furthermore, the PR is often less adhesive than different kinds of polymers, such as PDMS, allowing for a lower imprint pressure to be used [7]. Lower viscosity resistance makes it simpler for the liquid to fill the mould cavity without the need of suction. Zhou et al. used UV nanoimprinting to produce a polymeric membrane with nanoscale holes, using high-thickness PDMS nanopillars [8]. The high thickness PDMS nanopillars were supplied by projecting hPDMS from a nanoporous pAAO layer. Yanagishita and colleagues have demonstrated a technique for image nanoimprinting that produced an extremely uniform pore clusters polymeric pattern of about size equal to 100 nm by using a Ni nanopillar form, which is made of pAAO membrane (Figure 1). Then, the Ni form was loaded with PAK-01 (photopolymer monomer) and put on a glass substrate to initiate the polymerisation process in presence of UV radiation [9].

Figure 1 (a) SEM images represent the top view of the Ni nanopillars mould, (b) cross section, and (c) top view and (d) side view of porous Nickel mould with high porosity, reproduced with the permission from IOP Science [9].

The permeable polymeric membrane was carefully removed from the Ni mould, which had been pre-treated with a release agent. Despite the previously stated nanoimprinting advantages, the manufacturing of free-standing porous membranes is still a challenge since an extremely thin layer is often present at the bottom portion of holes. And membrane detachment from the substrate may also cause harm to the membrane. To resolve these problems, a sacrificial layer is placed in between the polymer and the substrate. Choi and colleagues used the UV nanoimprinting technique to create an underlying membrane detachment of 10-13 nm holes [10]. A sacrificial LOR layer of about 100 nm thickness was spin coated below the resist to make an SU-8 film. Conical holes were created and penetrated the sacrificial LOR layer via the film layer (SU-8) Following that, a polymer reflow procedure reduced the diameter of a pore to less than 10 nanometers.

2.3 Thermal nanoimprint lithography (TNL)

It is a kind of lithography that uses heat to create a thermoplastic polymeric thin layer which is maintained onto a strong substrate above its glass transition temperature (T_g) to allow decoration of a specified master mould with optimum pressing factor and time and also to mollify the layer [11]. At temperatures below T_g , the thermoplastic polymer's protection against flexible distortion and the esteem pressure where thermoplastic polymer deformation occurs both decrease substantially. Overheating, on the other hand, may damage the film [12]. After that, the engraving temperature is decreased below T_g which cause solidification of the thermoplastic layer. One of the most noticeable advantage of TNL versus PNL is the availability of a broad range of thermoplastics for the former. It's also essential to note how easy it is to regulate the thickness and uniformity of these thermal supports by spin coating them on a substrate [4]. In thermal nanoimprinting, a hard Ni structure is often used as a master shape, specifically for nanopore creation, since elastomeric forms, such as those constructed of PDMS, fail to meet expectations.

2.4 Tracks etching technology (TET)

Analysts can provide layers with perfectly regulated and consistent pore size, shape, area, and thickness using micro and nanofabrication processes based on track etching. The procedure's most notable advantage is that TET provides a broad range of pore sizes with high densities, starting from nano to microscale, that can be regulated autonomously.

TET, first described in the 1960s, works by lighting polymers with powerful X-beam irradiation, heavy ions, UV light and electrons causing straight damaged tracks to form through the exposed polymeric layer. To transfer the damaged tracks into pores, either an applied electric field or a wet chemical etching conditions are generally followed [13]. The use of heavy ions allows for a wider range of direct energy transfer of track-framing

particles, pore channel point circulation, and pore length [14]. A specific single light setup includes a magnetic defocusing instrument, a trigger, a sample stack, and an electrostatic deflector a detector as shown in Figure 2 [15].

Figure 2 Track etching setup using a single irradiation. reproduced with the permission from Beilstein Institute for the Advancement of Chemical Sciences [15].

To begin, the ion magnetically defocuses and alters such that a single beam of a particular frequency of a single beam passes through the aperture. The ion illuminates the stack of foils a short time later. The particles are identified by a solid state particle detector installed behind the test, and when a single ion is detected, the whole beam of ions are deflected by the electrostatic force of the chopper [16].

2.5 Other soft lithography methods

There are a few other types of imprinting techniques outside the two main nanoimprinting processes. Le et al. described a unique method for fabricating a porous PDMS membrane using two photoresist sacrificial layers (Figure 3).

Figure 3 Synthetic procedure of free standing PDMS layers and their top and side view in optical and SEM images, reproduced with the permission from Royal Society of Chemistry [17].

This research includes spinning of a positive photoresist layer as a sacrificial layer onto a silicon wafer. A very thin Titanium layer was sputtered on the photoresist layer. This results in prevention of the intermixing of the first and second photoresist layer [17]. Standard photolithography was used to create perfect instances of nanopillars on the following photoresist layer. The exterior of the nanopillar displays were then spin coated with a PDMS arrangement in hexane. The supported membrane PDMS was etched in a mixture of oxygen and sulfur hexafluoride to reduce the membrane thickness and to create the pores throughout the layer. Despite the fact, for soft lithography the material like PDMS has likely been the most often used because of its flexible surface chemistry, biocompatibility, compound dormancy, low cost and biocompatibility [17,18]. Research has been going on using different varieties of polymers. Yanagishita et. al. submerged a Ni nano array produced out of pAAO layer in monomers of benzoyl peroxide and methyl methacrylate arrangement of about 2 wt. percent, then polymerized it for 12 hours at 50°C to create a PMMA membrane [19]. After that, acid dissolution with Ni mould results in a free-standing membrane. This created membrane exhibited a width of 4.5 m a pitch distance of 500 nm, and pore width of 320 nm that were identical to the master mould

membrane of pAAO, which had a pitch distance of 500 nm, a thickness of 4.5 μm and pore width of 300 nm. This small difference in measurement of pore between the two layers e.g. (pAAO, PMMA) was believed to be due to shrinking of the PMMA volume during polymerization. This technique has the benefit of being able to create the nanoscale holes having high aspect ratios and that is hard to do with nanoimprinting which are pressure-based. This projection technique may also avoid producing a thin layer which is present at the bottom of the pores. With poly(ϵ -caprolactone) (PCL), Bernards et al. used the projection method to produce a nanoporous material which can be biodegraded. A ZnO layer was combined with ZnO nanorods as a layout, and the PCL arrangement was cast. A porous film having nanoscale pore size was created by etching the zinc oxide nanorods (having approximate length of 500 nm and width of 237 nm) with H_2SO_4 . The pore size and thickness of the produced PCL film were 21 nm and $5 \times 10^9 \text{ pore cm}^{-1}$, correspondingly. This methodology creates layers with a broad range of pore diameters and thicknesses, that has been used in a variety of applications, such as tumour cell separation [20], nanoparticle exhibit fabrication [21], and biosensing [22].

2.6 Self-assembly of polymers

Polymer self-assembly creates transparent polymeric films by causing polymeric precursors to spontaneously associate in response to explicit non-covalent interactions [23]. A phase inversion technique may often trigger self-assembly. Thermally induced phase separation (TIPS), vapour induced phase separation (VIPS), and solvent induced phase separation (SNIPS), are all noteworthy phase inversion processes. By manipulating the self-assembly routes, the macroscopic shape of the polymers may be successfully tuned, ranging from spherical colloidal particles to colloidal gels with hierarchical porosity. The resultant materials exhibit unique microporous characteristics due to the interior chamber of SNIPS. This synthetic method may enable the creation of soft, flexible materials that retain their porosity indefinitely.

2.7 Self-assembly of block copolymers (BCP)

For many decades, block copolymer (BCP) self-assembly has attracted considerable attention due to its ability to generate ordered structures with a wide variety of morphologies, having spherical, vesicular, cylindrical, lamellar, bicontinuous arrangements, and a variety of hierarchical or complex architectures. These self assembled polymers have prospective or practical uses in a wide variety of areas. Nonetheless, this technique is very beneficial for delivering permeable inorganic compounds i.g silica and carbons [23]. To begin with, block copolymers should be amphiphilic for the most part, with one portion which can interact with the prepolymer in a non-covalently manner. Secondly, this prepolymer should have the ability to cross-connect further forming a stable

system with no effect on the BCPs. Furthermore, easy BCP removal is essential without affecting the system structure [24]. The most important prepolymers in the development of the permeable frame are phenolic tars [25,26]. The fabrication of a 2D hexagonal mesoporous polymer sheet was disclosed by Schuster et al. The triblock copolymer (Pluronic P123) template was used to create an oligomeric precursor, followed by removal of BCPs. On a Si wafer, an ethanolic solution of precursor with BCP was coated. Circularly moulded pores of larger diameter = 6.8 nm and shorter diameter = 3 nm were found in the produced polymeric film. Liang and colleagues have developed a comparison approach based on PS-P4VP (polystyrene-block-poly(4-vinylpyridine)) self-assembly [27]. This method's distinctive feature is the incorporating monomers of resorcinol to the PS-P4VP BCP to give a base permeable design prior to resorcinol polymerization and carbonisation. This helps the BCP-resorcinol complex formation, resulting in excessive cross-connected resorcinol-formaldehyde tar that is sometimes hard to dissolve. The volume of the PS entity in the BCP may control the pore width, and the thickness of the pitch region can be controlled by the amount of resin used.

Block copolymer can also be used as a porous membrane framework where to construct the permeable film system by removing just one portion of BCP and, at times, some additional portions. One of the challenges in framing highly organised permeable polymeric membranes is to control the orientation of the pores perpendicular to the substrate all over the membrane. It is possible to tune the pore size of a membrane with systematic consideration of the proper experimental conditions such as parameters of kinetics of phase separation and film formation to achieve the targeted morphology [28,29].

2.8 3D printing technique

Added material manufacturing, often known as 3D printing, is one of the unique techniques which promises a vast production of membranes used in biomedical applications. The capability to create complicated forms or components in three dimensional methods using varieties of materials, such as graphene-based materials, ceramics, metals, conventional thermoplastic of different scales [30], is the greatest advantage of this technique. This technique is classified into four categories: (1) photo polymerisation, which involves restoring photoreactive polymers using a laser or UV light [31]. (2) powder-based printing, where an ideal material's powder is placed on a substrate which follows a binder material spurting and selective sintering to get a 3D material [32], (3) material extrusion, which softens and expels a polymeric material fibre to form an optimal structure when heating the thermoplastic over its T_g [33] and (4) a desired 3d shape is achieved by lamination of the thin layer of the materials [34]. Stereolithography (SLA) is a polymerisation technique based on the laser light based lithography that has got wide applications for production of

polymer based membranes currently. In this process an UV laser follows the optimum design and attaches the photoresponsive polymer on the bottom/ top part of the stage in motion. When the perfect decoration is created on the stage it is vertically dropped on the surface of the resin followed by curing by the UV-laser to form a consistent 3D item (Figure 4) [35].

Figure 4 3d Printing by stereolithography showing in normal as well as inverted mode, reproduced with the permission from Wiley-VCH [35].

However, 3D printing has enormous promise in a variety of areas, including design, assembly, manufacturing and medicine design, it is still with major drawbacks such as printing resolution, microscale pore formation [30,35]. Producing membranes with pores in nano range is still a great challenge. Although most three dimensional printing methods have a microscale target limit, the late advancement in the use of the TPP(two-photon polymerisation) technology for three dimensional printing has shown the potential to reach as far as feasible to a 100 nm scale. While this technology has progressed rapidly over the past decade, it still faces a few challenges: (1) maximum production costs, (2) lower stability of final material without proper treatment, and (3) types of material used. According to literature, there have been few reports of 3D printing being utilised to produce permeable polymeric sheets with pore size in nano range. But we believe this technology will pave the way for the potential production of permeable films in future.

2.9. Electrospinning (ES)

Porous polymeric structures when synthesized by electrostatically operated spinning of polymeric fibres is called electrospinning. This method may produce permeable polymeric films with pore diameter ranging from micro to nanoscale. High pore interconnectivity, adjustable thickness, high gravimetric porosity, interstitial space in micro range, high surface to volume ratio and a low thickness with good mechanical property in terms of strength are all advantages of such layers [36].

Figure 5 Schematic procedure of electrospinning technique, reproduced with the permission from Wiley-VCH [37]

Figure 5 shows an average electrospinning measurement. The pre-arranged polymer arrangement is first softened or disintegrated in solvent and then positioned into a capillary tube in this method. Then, an electric field strength is employed in between the collector and tip of the capillary. The developed charge is in opposition to the surface strain of polymer fluid held at the tip of the capillary. The hemispherical condition of polymer liquid at the tip transforms into a cone-shaped structure termed Taylor cone as the electric force is increased. The arrangement is launched from the tip of the Taylor cone when a critical value is induced by the applied electrical field that exceeds the surface pressure of the polymer fluid. Electrically controlling the path taken by the charged jet of polymer solution

allows uniform polymeric fibres to be collected to produce permeable membranes [36]. In general, there are two types of electrospinning: (1) solution electrospinning (SES) and (2) melt electrospinning (MES).

2.9.1 Solution electrospinning (SES)

SES is a mostly used and well-established technique that can be easily handled at 25°C. Ambient system parameters, solution, and process are the three main entities that govern the electrospinning interaction. The electrospinning process is influenced by environmental factors such as temperature and humidity. Ray et al. discovered that high humidity inhibits polymeric solution elongation, resulting in an increase in nanofiber diameter [38]. Where as according to Mit-uppatham et al. high temperature results in the synthesis of thin fibres [39].

Table 1 Various preparation procedures and materials used.

Preparation Technique	Materials Used	References
Nanoimprint Lithography	hard polydimethylsiloxane (hPDMS)	[4]
Photo nanoimprint Lithography (PLN)	porous anodic aluminium oxide (pAAO) + Ni metal	[9]
Thermal nanoimprint lithography (TNL)	Thermoplastic polymers, Ni substrate	[11,12]
Tracks Etching Technology (TET)	powerful X-beam irradiation/ heavy ions/ UV light on polymeric membrane	[13,14]
Self-assembly of polymers	PS-P4VP (polystyrene-block-poly(4-vinylpyridine))	[24, 27]
3D printing Technique	Organometallic polymers, Resin, Ceramic, Metals, Conventional Thermoplastic Polymers	[32-34]
Electrospinning (ES)	Poly ethelene glycol, Synthetic/Natural polymers, Chitosan	[36,37]

2.9.2 Melt electrospinning (MES)

MES uses a simple cleaning method to remove the solvent after fabrication, and there is no need to choose a solvent. It's best for polymers that don't have a suitable solvent to dissolve

at 25°C. Do and co-workers used dissolved coaxial electrospinning to make polyethylene glycol shell nanofibers [40]. This technique allows for changes to the film geometry, such as tube form, as well as the precursor selection from a broad variety of polymers, such as natural and synthetic polymers having biocompatibility [41]. Tissue engineering, drug delivery, water purification, and lithium ion battery technology are only a few of the applications of the membranes created by this process. The significant surface roughness of these films encourages surface fouling, making them unfit specifically for biosensing applications. The Synthetic Techniques and the materials used in various process are summarised in Table 1.

3. Applications of porous membranes

3.1 Pressure-driven membrane processes

Depending on the desired separation, membranes can be used to (1) remove pollutants from waste streams so that the water can be recycled or discharged, or (2) concentrate or recover necessary components while the remainder is allowed to flow through the membrane. Both activities are crucial because they may help to accomplish two objectives in many industrial processes: (a) water reuse and (b) raw material or (by)product recovery. To remove particles in the 0.05–10 mm range, MF employs porous membranes with pore sizes in the range of 0.05–10 mm are used. Particles are kept depending on their dimensions in this filtering process (shape and size dependent). This membrane technique most closely resembles conventional coarse filtration (Figure 6). [42]

Figure 6 Pressure driven membrane processes.

Although polymeric materials make up the bulk of MF membranes, inorganic materials such as aluminium (Al) oxide, zirconium (Zr) oxide, titanium (Ti) oxide, carbon, silicon carbide, and other metals are also frequently used (steel, tin, nickel, etc.). MF may be used in the purification (e.g., of fruit juices, wine, and beer), sterilisation (e.g., of drinks and medicines), or concentration phases (e.g., in the cold sterilisation of beverages and pharmaceuticals) to retain suspended particles (i.e., in cell harvesting). In the production of drinkable water from ground water using NF and RO, MF is also used as a pretreatment step [43,44]. Ultrapure water production from the semiconductor industry, metals recovery as colloidal oxides or hydroxides, wastewater and surface water treatment, and oil–water emulsion separation are some of the other technological applications. Large molecules, having dimensions in the range of 2–100 nm (proteins, polymers, colloids, and emulsions) are kept in UF. Small molecules, such as salts and organic solvents, as well as low-molecular-weight solutes, may pass easily across the membrane. The separation is based on a sieve process, similar to MF. UF membranes may be made of polymers or inorganic materials, much as MF membranes (mainly Al and Ti oxides). UF is used as a concentration/purification step in the dairy (milk and whey processing, and cheese manufacturing) and food industries (i.e., in the production of potato starch, and protein recovery and hydrolysis). It is also used in the metal and surface industries (for oil–water emulsion treatment and electropaint recovery), the textile and automobile industries (for indigo recovery), and wastewater treatment. NF is a membrane method that retains low molecular weight organic molecules (200–1000 Da) as well as multivalent ions like sulphates in a size range between UF and RO. In contrast to RO, the pressure utilised is modest (in the range of 3–20 bars), yet substantial fluxes are obtained. To separate particles in NF membranes, particle size, particle charge, or a combination of both may be employed. The majority of NF membranes are now polymeric composites; nevertheless, a growing number of NF ceramic membranes with unique separation characteristics are becoming available [45]. In water softening (calcium ion removal), solvent recovery, and wastewater treatment, small compounds including proteins, enzymes, antibiotics, dyes, herbicides, pesticides, and insecticides are frequently removed utilising NF methods. Low-molecular-weight compounds, like salts, may be retained using the RO method. Organic solvents, on the other hand, have a low retention rate because they break down quickly in the membrane. cellulose triacetate, aromatic polyamides, and polybenzimidazoles are the most prevalent RO membrane materials utilised. Ceramic RO membranes are currently not available in the market. Desalination of saltwater; ultrapure water manufacturing (electronic industry); concentration of food juice, sugars, and milk; and wastewater treatment are the primary uses of RO [46].

Membranes are used in a variety of industrial applications that need system stability, high accessibility, low requirements for preventive maintenance, and minimal care. For such demanding applications as those found in the chemical and pharmaceutical industries, as well as those found in water and wastewater treatment, ceramic membranes have emerged as the preferred choice due to their extremely high chemical and physical (thermal and mechanical) stability, exceptional separation features, and extended operational period. When compared to other membrane types utilised in pressure driven membrane methods, the following are the most often mentioned benefits of ceramic membranes: The operating life is lengthy and consistent. They show high temperature resistance (up to 300 °C, depending on the material) throughout the pH range, and pressures up to 30 bars (generally they withstand up to 90 bars). The stability in various chemical environments is excellent (i.e., oxidants, hydrocarbons, organic solvents, and including acids like hydrofluoric/phosphoric acids when pure titania is used), bacteria resistant and, in many instances, bioinert compatibility with highly viscous liquids resistance to corrosion and abrasion. In addition better sterilization and cleaning properties under chemical or steam with back flushing are also shown. Because of these properties, they may be used in a number of applications where polymeric and other inorganic membranes are ineffective. Membrane pore diameters in the MF-UF-NF range may now be found in a variety of sizes (from 5 mm down to a few hundred daltons). Cleaning under chemicals at high temperatures using chlorine, ozone, hydrogen peroxide, and robust inorganic acids, caustic, as well as steam sterilisation, are also possible with ceramic membranes. Owing to their exclusive properties, ceramic membranes (CMs) may be cleansed simply by backpulsing. In this process the flow over the membrane is reversed. As a consequence, the filter cake is driven aside from the surface of the membrane, extending filtering efficiency and reducing cleaning downtimes. Most ceramic membranes have much greater permeability rates than presently available polymeric membranes. In most applications, good organic retention and a low fouling propensity have been verified. Salt rejection, on the other hand, reduces dramatically when electrolyte concentration increases, as it does during the treatment of pickling bath solutions. As a result, using ceramic NF membranes in such a medium isn't always a good idea. Ceramic membrane rejection, on the other hand, is less temperature sensitive than polymeric membrane rejection (Considering both the average cut-off and the size distribution), which may be a benefit in certain applications. The hefty weight and high production costs of ceramic components are the two biggest disadvantages. Nevertheless, in situations where polymeric membranes are not possible, they usually have a lengthy service life. Furthermore, they may be recoated in the case of membrane loss, lowering element (membrane) replacement costs [46]. CMs were first created for uranium enrichment, but they were later utilised in wastewater treatment as well. Various industries like food, chemical, petrochemical, biotechnology, pharmaceuticals, dairy, and metal

polishing as well as power generation are all using ceramic membranes. Each industry has its own set of needs and opportunities [47]. Aside from industry-specific applications, a few common techniques are utilised across a variety of sectors. Oil/water separation and cleaning chemical recovery are two examples [48-50]. There are many examples in the food industry, metal fabrication and allied industries, automotive sector, chemical manufacturing sector, and oil refinery, among others, of petroleum oils from container washers, spills, drilling, and other processing operations. CMs are used in wastewater treatment for a variety of purposes, including oil removal from wastewater or purifying washed water from metal or textile cleaning, pre - treatment of landfill effluent. The benefits of CM may also be seen in recycling technologies including enamel, coating, and paint recycling, petrochemicals recycling, and degreasing cleaning baths. Emulsified oils in the wastewater are difficult to separate using traditional treatment methods like coalescers and oil skimmers. Furthermore, many polymeric membranes are inappropriate in hostile chemical conditions, such as heavily polluted oily wastewater, owing to their low stability (e.g., petroleum fractions, lube oils etc). On commercial scale systems fitted with back pulsing devices, long-term flux stability has been established (300 liter/m² h was reported for the handling of generated water comprising 10–100 ppm suspended particles and oils using 0.8 mm Membralox membranes over many months) [51]. Chemical recovery varies by location, but on average, 95 percent of the active chemical solution is recovered, with Kjeldahl nitrogen rejections of up to 75 percent, 97 percent oil and grease rejections, and 100 percent suspended particles rejections. Many factors influence the payback, including the characteristics of the discarded cleaning solution, the cost of new chemicals, the percentage of recovery, the number of times the permeate may be reused, as well as utility and waste disposal costs. However, it is typical to have a payback period of less than a year or two [52]. Ceramic MF membranes are also often used in the processing of various water sources prior to RO. Ceramic membranes provide consistent performance under substantially changing feed circumstances in this application, and as a consequence, RO membrane lifespan may be doubled or tripled [52]. Recovery of catalysts, recycling of brine, colored and pigmented dyes and pigments may be recovered. Desalination of products is a process that involves the removal of salt from items (i.e., optical brighteners, surfactants, and dyestuffs). Organic solvents are cleaned, recovered, and recycled (solvent NF) by using porous membranes.

3.1.1 Textile/pulp and paper manufacturing

Processing of fuel oil and ethanol, fractionation of linosulfonates, COD reduction of bleach plant effluent, recovering whitewater from paper mills, recovering the coating on paper, rinse water from main and secondary wool scouring effluent, are some of the applications of porous membranes. The loss of colour, high-quality water for recycling, recovering and

reusing dye baths, finishing the spin bath water recovery is aided by the use of a water jet loom are done by utilizing porous membranes.

3.1.2 Biotechnology, pharmaceuticals, and cosmetics

Pharmaceutical active agents (antibiotics, enzymes, proteins, amino acids, and vitamins), as well as plant extracts, are concentrated, fractionated, isolated, and sterilised, biomass and algae separation, concentration, and dewatering, filtration of blood plasma, fat emulsions disposal, Clarification of fermentation broth, yeast separation, and bacterial suspension concentration, getting rid of endotoxins, recovery of aqueous stream byproducts, production of vaccines, nutraceuticals, are performed by ceramic membranes.

3.1.3 Surface engineering/automotive/mechanical/mineral/metal industry

Degreasing and rinsing of baths, treatment of emulsions of oil and water, heavy metals' resurgence, wastewater from grinding operations, glass/glass fibre manufacturing, wastewater treatment and, removal of oily wastewater are some of the examples where porous membranes are widely used.

3.1.4 Foodstuffs, dairy products, and beverages

Wine, beer, cider, soy sauce, and vinegar purification, juice concentration, microorganisms are removed from milk and whey. Milk and whey components are separated and fractionated. Whey desalination, soybean protein separation, processing of vegetable oil, drinking water purification, processing of sugars and starches, product recovery from beer and cider tank bottoms, water recovery from the waste stream are some of the application of porous membranes in above mentioned industries.

3.1.5 Water, recycling, and the environment

Treatment of wastewater and potable water, membrane bioreactors reduce COD, BOD, and suspended solids, chemical recycling and washing wastewater (i.e., laundry), waste oil treatment, emulsified oil removal, pesticides and drugs removal, getting rid of germs, heavy metals removal, treatment of grey water, sewage plant /sewage drain purification, water recovery from methane digesters, vacuum residual oil upgrade, processing of landfill leachate, treatment of radioactive wastewater are some of the application of porous membranes.

3.2 Chemical and petrochemical industries

The chemical industry is very diversified, using all main process technologies. There is a requirement to (1) recover and reuse chemicals in various chemical process applications,

and/or (2) treat highly variable wastewaters including detergents, polymers, and organic solvents. However, there is a growing need for better product quality, faster payback periods, and lower operational costs. Membrane technology is becoming more popular as product separation gets more complicated. This is especially true in the fine chemical sector, where membranes are employed in a wide range of applications, including the concentration and desalting of dyestuffs and optical brighteners, for example. Ceramic membranes, which can function in more severe circumstances such as high temperature (over 200 C), high/low pH, and solvent resistance, may provide substantial benefits over more traditional technologies in such a situation [53]. The following are some of the most common ceramic membrane uses in the chemical industry today: Recovery of pigment, hydroxide, and catalyst. The recovered product is recycled back into the process stream, and the resultant wastewater's chemical oxygen demand (COD) is substantially decreased. Desalting is the process of removing inorganic particles from powder and liquid dyestuffs during production. The membrane rejects the dye while allowing salts and water to flow through, concentrating and desalting the dye at the same time. In the manufacture of powder dyes, NF may be used to improve plant capacity prior to drying. In the production of liquid dyes, the dye's solubility is improved by nearly full desalting. Concentration of silica sol and latex membrane technology offers a cost-effective way to concentrate latex white water with up to 15% solids. After that, the latex may be recovered, and the cleaned water can be reused. While aqueous membrane applications continue to dominate the market for pressure-driven membrane processes, emerging solvent-resistant NF membranes open up new possibilities in the chemical sector [54]. Separation of oil and water, most governments have certain standards for the quality of wastewater when disposing of mineral oil in surface water and sewage systems. A significant quantity of oil may be extracted from wastewater using a water-oil separator. Chemically stabilised oil/water solutions, on the other hand, must be handled carefully. Membrane filtration may be used to purify these solutions, resulting in dischargeable water. Oil/grease 136 ppm to 1 ppm, Pb 0.79 to 0.09, Ni 0.15 to 0.01, Cu 1.49 to 0.36, and Zn 5.9 to 0.37 are typical findings from waste stream to permeate [55]. Ceramic membranes are often used as an intermediate filter or prefilter for more costly RO membranes, as well as for the reduction of oily bilge wastes, process wastes, and wash water wastes. Pretreatment with RO. Backpulsing allows ceramic membranes to be cleaned continuously in situ (CIP), reducing the requirement for off-line cleaning. As a result, ceramic microfilters lower the cost of replacing ROs. The amalgam process produces sodium hydroxide (50 percent by weight), which is loaded with mercury downstream of the amalgam decomposer in chlorine-alkali facilities. Filtration using ceramic membranes may remove this mercury, as well as other solid contaminants like graphite.

3.3 Porous membrane in biomedical applications

Nanoporous materials offer several potential biological uses that are presently being investigated. The membrane in implanted devices will behave as a semipermeable section which would keep the material or components in place and allows for the controlled release of necessary molecules. Nanoporous membranes (NPMs) may also be used for biomolecular analysis in a number of ways. In vitro uses include protein separation and diagnostics. Significant research has been conducted over the past decade to automate biological testing and reduce the amount of time and money spent on sample collection and analysis. These efforts have resulted in a large number of microfabricated devices that perform mixing, detection, reaction, separation or preconcentration functions. It has been shown that the alteration in selective transport and diffusivity across the membrane may be utilised to extract analytes from complex mixtures. Lab-on-a-chip concepts have garnered a great deal of interest in recent years [56]. The current section explains an overview of NPMs and their use in biological applications. While the applications are divided into categories depending on how the membrane functions, there is considerable overlap between the categories.

3.3.1 Biomolecule separation and sorting

In various fields, such as the pharmaceutical industry, the food industry, and biotechnology, separation and sorting are vital because they are used to separate and purify molecules from a variety of biological feed streams. Separation and sorting are also important in the food industry. Separation science makes use of a number of techniques, such as size exclusion chromatography and biopolymer gel electrophoresis [56,57] to separate molecules. In recent years, researchers have been looking into the separation of biomolecules in more organised holes for a range of applications. During kidney application, a synthetic NPM acts as a supporting entity for renal cells as well as a filter for blood, keeping important molecules like serum proteins and releasing smaller waste particles to flow through it [58]. The regulation of the flowing materials through the nanopores may be done from outside. For instance, Martin and colleagues have developed a membrane composed of an assembly of cylindrical gold nanotubules having a pore diameter of less than 1 nm that may be used as a sensor [59]. They demonstrated how, simply changing the charge in the nanotubules (positive to negative), enabled them to refuse ions with opposite charges, permitting for voltage gating of molecules with opposite charges.

3.3.2 Biosensing

Sensory systems detect substances and enable cells to respond to stimuli via a variety of protein pores that are linked with the membrane. It is possible to utilise this kind of biosensing in several technical fields, comprising the medical diagnostics, pharmaceutical industry, and the detection of potentially harmful biomolecules, among others. A biological component is used in conjunction with a physico-chemical recognition unit in the majority of these applications to distinguish analytes in biological systems, and the biosensing device is used in these applications. Electrochemical sensors, such as amperometric sensors, are devices that utilise an immobilised enzyme to convert targeted analytes in a biological feed stream into products which can be detected electrochemically. The most common method that is being used for assessing blood sugar levels is the fasting glucose test. Researchers have shown that glucose oxidase immobilised on a porous nanocrystalline TiO_2 screen is capable of detecting glucose in the blood [60]. A similar approach has been used to develop cholesterol biosensors based on immobilised enzymes (cholesterol oxidase) inside ZnO nanoporous thin films [61], which detect cholesterol levels in the blood. It is also important to mention the amperometric-type enzymeless nanoporous systems that have been developed. In recent years, researchers have demonstrated a system for sensing glucose that uses an electrode of nanoporous platinum. This miniaturised electrochemical cell was implanted in a microfluidic chip consisting of a network of microfluidic transport channels [62]. Bohn and his coworkers proposed a nanocapillary membrane based PTAS devices which are electrically actuable, to perform analytical operations and sensing. It may reduce the number of constituent parts in the sensing device [63]. Another category of NPM based biosensor, which analyses samples at a single molecular level at a time. The next section offers a well description of these important materials.

3.5.3 Analysis on a single molecular level

Nanoporous supports have become more popular for single-molecule analysis because they allow researchers to probe biomolecules (proteins, RNA, and DNA) one at a time. For example, it has become well established in recent years that determining the size and frequency of blockages in an electrolyte's ion current when the biologically active molecules are brought through nanopores integrated in insulating membranes can provide information about the structure, concentration, size, and sequence of single-stranded RNA or DNA, among other things. This method has been utilised by manufacturing specially designed receptors on membranes. For example α -hemolysin (cc-HL) protein integrated in a lipid membrane to detect biomolecules [64]. In the early days of analysis of single molecules, lipid membranes embedded in microporous film of polymers like teflon were

used in many of the experiments. In addition, it was the fact that the microporous membrane support needed to be further improved for practical applications, as the lipid membrane was unstable and ruptured after a shorter time span, which was one of the major drawbacks. It was suggested that the protein pores can be supported using nanoporous membranes [63]. The design of the protein pores restricts the number of sensing applications that can be implemented using lipid-bound nanopores. Synthetic nanopores have recently been explored as a means of improving the functionality of single molecule detectors, according to the researchers. Artificial nanopores constructed from a variety of materials, including glass, polymers, and solid-state membranes, have been used to detect DNA of both type (i.e. double-stranded and single-stranded), ions, proteins and macromolecules. Analyte-surface interactions may be controlled by nanoscale manipulation of synthetic nanopores, allowing for the development of sensors with desired functionality. Arrays of these sensor platforms with a range of analyte sensitivities, which can be combined into microfluidic devices [65], may be used to create lab-on-a-chip technology.

3.3.4 Immunoisolation

It is the technique of preventing an immune response from harming implanted cells or drug release systems that is known as immunoisolation. It is the most popular technique to encapsulate materials with the use of a nanoporous semipermeable membrane. Using nanoporous membranes, it is possible to protect transplanted cells from being attacked by the immune system of the body. These membranes have pore size suitable for permitting the minute molecules like oxygen, insulin, glucose. At the same time also small enough to block the bigger chemicals present in our immune system such as immunoglobulin, which are present in huge quantities. Such immunoisolating devices act as a semipermeable membrane in artificial pancreas. According to researchers these devices act as an interface between the body fluid and insulin releasing pancreatic cells.

According to Desai et al., the application of microfabricated nanoporous silicon interfaces in implantable artificial pancreas for the treatment of diabetes was explored [66]. The desirable properties of these nanoporous membranes are biocompatibility and resistant to biofouling in order to be used in a variety of in vivo applications.

3.3.5 Drug distribution

The invention of in vivo delivery techniques to enable for the controlled distribution of drugs locally where they are needed is now being explored by the pharmaceutical industries. In order to provide more effective therapy while also reducing the danger of wrong dosage, controlled delivery systems are desired. When the pore size, porosity, and

thickness of nanoporous membranes are all regulated to a high degree, they offer an attractive approach for creating capsules that may be used to deliver pharmacologic compounds with controlled release [67]. As an example, nanoporous materials are being investigated for their potential use in drug-eluting stents for the treatment of coronary artery disease [68]. The use of nanoporous inorganic membranes for the continuous administration of ophthalmic drugs to treat eye disorders has lately been investigated [69]. When linked to biosensors, smart food delivery systems that respond to physiological changes are possible.

Conclusions

Porous polymeric membranes are considered a hot field of research in recent separation based technological applications. Materials and manufacturing techniques of these porous polymeric membranes were briefly explored in this chapter. Polymers with high mechanical strength and cheap cost were observed to gain high importance. The favored method for producing porous polymeric membranes with controlled shape and performance was also discussed. It covered the system, solution, processing, and the surrounding environment. Despite this, certain issues need to be addressed in future research. Investigation on more efficient and less expensive manufacturing methods are the present need of modern industrial applications. The use of various types of porous membranes may have the potential to replace energy-intensive distillation techniques for separation of organic solvent as these are fast and cost-effective. On the other hand, nanoporous materials are more favored for biomedical applications. Controlled pore size distribution, high porosity and low thickness, mechanical and chemical resistance are the essential requirements for selective membranes. True nanoscale devices need to maintain precise pore distribution and molecular sorting. Implantable device membranes must be biocompatible and biofouling resistant. Currently, inorganic, or organic compounds are coated onto nanoporous membranes to impart chemical and mechanical stability. The responsiveness of nanoporous membranes is currently being investigated in labs for biological applications. Smart membranes may be programmed to interact with various physiological environments like pH, temperature, and ion concentration. Making multi-responsive nano-porous composite membranes is the recent challenge in membrane technology which needs to be solved to an early date.

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