Chapter 1

Polymer-Based Membranes

Ashok Shrishail Maraddi and S.K. Nataraj^{1,2,*}

¹Centre for Nano and Material Sciences, Jain University, Jain Global Campus, Bangalore-562112, India

²IMDEA Water Institute, Avenida Punto Com, 2. Parque Científico Tecnológico de la Universidad de Alcalá, Alcalá de Henares, 28805 Madrid, Spain

* sknata@gmail.com; sk.nataraj@jainuniversity.ac.in

Abstract

Membrane science and technology is increasingly playing an important role in maintaining environmental health. Polymer based membranes in particular show great potential in removing environmentally hazardous pollutants from the wastewater. Membrane technology has also been widely used for ground, surface and seawater desalination which is serving the humanity by providing high quality drinking water. Polymeric membranes have been categorized based on their pore size and their distribution which make them tailor made and innovative separation media namely, reverse osmosis, nanofiltration, ultrafiltration, microfiltration and forward osmosis. All these membrane process require high performing membranes as separation media. This chapter give detailed account of membrane preparation techniques, membrane modules and their applications in different fields. Further, the ideas covered in this chapter are fundamental to all membrane processes. Transport processes, membrane preparation, and flow separation effects are just few of the topics that have been studied.

Keywords

Membrane Technology, Polymer Membrane, Advanced Membranes, Functional Polymer

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Today, the membrane technology is a front runner among several existing separation and purification technologies due to its rapid separation and purification characteristics and ease of adaptation. Membrane science and technology has been constantly evolving over several decades now. As it seem to always be the case, the membrane technology has also its origins in nature [1]. Early membranes were conceptualized by studying biological membranes and their functions as they have efficient mass transport properties. Membrane science and technology gained huge importance as one of the most important, useful and rapidly developing branches in engineering and industrial subject and is an expanding field finds wide applications in the field of research, development, engineering and manufacturing which includes synthesis of active pharmaceutical ingredients (APIs), dairy products, macromolecular separation, petroleum industry, desalination, water/ground water treatment, wastewater treatment applications, emerging pollutants removal, controlled-release of pharmaceutical formulations, gas separation, dialysis, artificial kidney etc. Hence, membrane science and technology connect different disciplines from manufacturing, separation, segregation to product recovery, solvent recovery and at the end waste treatment associated with all afore mentioned process steps via selective transportation of desired ingredients across membrane [2-4].

Membrane separation comprises with a variety of processes that can operate under a variety of physical circumstances and principles that can be adapted to separate miscible and/or immiscible natural components from a wide range of mixtures. Since, separation of selective component from mixture across membrane is purely physico-chemical in nature, the membrane's physical and chemical properties, along with the permeating components play crucial role in its separation efficiency. This influences the particular component transportation across the membrane more readily than other. Abundant available polymers have been adapted to prepare these membranes.

Historically, membranes have been conceptualized following biological mimicking membrane found in living organisms. To suit the different conditions, all initial membranes have been developed using cellulose-based precursors. The first evolution of membranes were prepared and tested by Loeb and Sourirajan in early 1960s using modified Cellulose Acetate [5]. The polymers extensively used for membrane preparation can be sourced from commercial market or prepared from different polymerization fundamentals like addition, condensation or by the copolymerization processes. Design and application of task specific membrane with defined pore structures, morphology and

their transportation mechanism depends on the various factors such as precursor used, method followed and the mixtures to be separated. In such case, overall membrane performance can be achieved with careful selection of types of polymers used, classification of membrane to be prepared, parameters to be controlled to tune porosity and the engineering the membrane to workable membrane modules. These all steps are inter-dependent and integral to each other. Defined pore sizes, their shape and distribution across the membrane plays very crucial role in different separation mechanisms and membrane transportation qualities. In general, in porous membranes, separation of one component from the mixture may depend just on differences in diffusivity and rate of diffusivity. A solution-diffusion mechanism is used to move or permeate liquid across dense or non-porous membranes. In specific condition, the transportation or penetration of liquid through membrane is determined by the chemical structure and nature of the polymer, as well as the affinity of a liquid, and the selectivity is determined by the solubility and diffusivity ratios, respectively. In dense membranes, the concentration and activity gradient in the provides the driving factor for liquid transport. However, in case of gas separation rate of gas diffusion of transportation can be influenced by increasing the upstream pressure, however pressure has a little effect on activity on the transportation of liquid phase.

With overview of vast sea of literature and the technological report of offering different advantages with respect to technical, economical superiority, it is evident that the membrane technology has been very successful method over the other existing separation technologies or it is considered to be the main path that has been adapted for separation and purification applications at industrial scale. Membrane technology has gotten a lot of consideration in the last two decades as a result of the global water crisis. Special emphasis has been on using polymer-based membranes as tools in water management and wastewater treatment related environmental engineering. With enormous technological advancements over a period of time, membranes in both pristine and composite forms has shown extremely important adaptability behaviors to the specific application. This gives membrane technology an economical advantage when used at industrial scale. Even though membranes have been in existence for over five decades, the increasing water scarcity and the water-related pollutions is driving the growth of this particular technology at an average compounded annual growth rate (CAGR) of 8% and the US market alone for membrane market growth is forecasted at CAGR of 6%. In all, Polymer-based membranes account for the majority of materials types employed in membrane preparation, as they are abundant in nature with simple preparation techniques to adapt, clean and engineer into different modules, that can be maintained well for its long

durability. Herein, the present chapter gives an overview of different polymer-based membranes prepared from different materials to their present applications.

2. Definition of membrane, structure and morphology

Membrane is as a semi-permeable barrier which selectively transport one or more component from the feed mixture. Semi-permeability nature of the membrane indicates its affinity for specific component of the mixture that can preferably be diffused or transported across the membrane. In general membrane can be prepared with different thickness and flexibility. Considering the end application and volume of mixture to be separated, polymer precursor, porosity required and the module suitable to handle the amount of feed can be optimized. The capacity of a membrane to control the penetration rate of a chemical species over the membrane is one of the key qualities utilized since membranes play such an essential role in chemical technology and are employed in a wide range of applications. The transportation properties of membrane are greatly influenced by feed conditions as well such as pH, temperature, operating pressure and the flow rates.

3. Types of membranes

Polymer-based membranes are a key component in a wide range of industrial applications, including water purification and, in polyelectrolyte form, fuel cells and batteries, where they control the selective transport of ions and/or water. The precise nature of ion and water transport is frequently confusing, because it is dependent on the complex interplay between polymer structures. Broadly the polymer-based membranes are classified as dense or non-porous membrane and porous membrane.

Dense membranes are generally prepared via (1) solution casting method whereas the porous membrane use (2) non-solvent induced phase separation technique (NIPS) and (3) temperature induced phase separation (TIPS) techniques. Advanced membrane preparation processes such as track-etching, stretching, electrospinning, or sintering have been developed in addition to traditional approaches to make membranes for specialized uses. In NIPS, the phase inversion of a polymer carried out via immersion precipitation of caste polymer solution using non-solvent. Here, the polymer solution is casted on a suitable support material, namely the synthetic polymer base, which is then immersed in a coagulation water bath, containing non-solvent solution. The solvent and non-solvent exchange that occurs during this coagulation exchange process results in the creation of porous polymer membranes.

Permeants or feed components are conveyed selectively via diffusion through dense membranes under the driving force of a pressure, concentration, or electrical potential gradient. The relative transit rate of distinct components of a mixture within the membrane, which is dictated by their diffusivity and solubility in the membrane material, is directly connected to their separation. Nonporous, dense membranes, on the other hand, can separate permeants of similar size if the concentrations of the permeants in the membrane material differ significantly.

3.1 Dense membrane via solution casting method

Figure 1 Schematics of dense membrane preparation route both in (a) free standing form and (b) supported dense membrane.

Dense membranes are employed for efficient separation with sufficient permeate flux in practically for all reverse osmosis, gas separation, pervaporation, and membrane distillation processes. Dense membranes further can be classified in to two types based on their physical characteristics namely; (a) free standing dense membrane and (b) supported dense membrane as shown in Figure 1. In solution casting method of self-supported dense membrane preparation follows, solution casting of polymer followed by evaporation, whereas supported membrane is prepared first support is prepared via dry-

wet immersion technique followed by dip coating or solution casting leading to complete solvent evaporation. Dense membranes usually with the thickness of 38-110 μm range. The separation here occurs mainly by a solution-diffusion process that includes numerous influencing elements such as temperature, pressure, polymer type, rate of diffusivity, and so on.

3.2 Symmetric porous membranes

Figure 2 Schematics of porous membrane preparation routes showing morphological features of (a) Symmetric and (b) asymmetric porous membrane.

Porous symmetric polymeric membranes prepared from phase separation generally with track etched support layer having high flow rates and selective layer with excellent retention properties as shown in Figure (a). These membranes are also prepared without separate selective layer from a metastable two-phase liquid dispersion of polymer in solvent and non-solvent systems.

3.3 Asymmetric membranes

In asymmetric membranes, pores are distributed in ascending order from bottom to top of selective layers. The tight pore size regime generally sits on the feed facing selective

layer. Among many polymers, polysulfone, polyethersulfone, polyacrylonitrile and cellulose-based systems are co-operative to formation of highly asymmetric membranes. In a classical asymmetric membrane, it is the surface pores that are the tight and the permeation channels are broad to facilitate the transportation of product/permeate as shown in Figure 2(b). In the asymmetric membranes the tightest pores are adhered to the interface of the supporting skin and the selective layer when used in composite polymers. This is also called skin and the asymmetric region of the composite membrane. Asymmetric or anisotropic (from support where the asymmetric region generally originates) regime mainly defined by the degree of asymmetry to be called as tight or loose type of asymmetric membranes. These membranes will have average skin sizes of greater than 1 micron in homopolymer type and varying sizes for composite membranes from NF to RO regime as shown in membrane spectrum in Figure 3. In general, The physical properties of the support layer or permeation layer will be at least twice those of the average skin pore size and thickness [6].

With the advancement of nanocomposite, membrane technology is too benefited by the use of different nanomaterials for membrane applications. Where, the top layer of an asymmetric membrane is functionally induced by different nanoparticles induced to form several selective layer films. In such cases, asymmetric membranes consist of a thin dense layer that can act as a selective skin as well as a porous support, the interstitial spaces generated between the composite layers in the Nano scale range functions as permeation channels. This engineering adaptation of the asymmetrical structure with a dense layer on top that is tight to thin and supported by a porous substrate is strategically crucial to improve separation efficiency. This will also reduction membrane resistance to permeate flow and improve the shelf life.

4. Preparation of porous membranes and control parameter

4.1 Solvent phase inversion technique

Polymer-membrane science and technology has progressed to the point where it may currently be used in a variety of separation processes, such as water desalination, macromolecular enrichment, and biological component cleansing etc. Synthetic polymer membranes can be made using a variety of procedures that allow for the shaping of a polymer material to achieve the required properties, the most essential of which are morphology, porosity, and distribution. Before casting solution, desired membranes characteristics need to be understood and accordingly precursors need to select. Two elements must be considered while producing polymer-membranes for a certain separation: That consists of 1) the nature of the precursor material (polymer or polymer

blend or composite polymers) and 2) the morphology (dense/non-porous or porous) of the membranes. Solution casting of polymer solution to turn in to either porous or non-porous membrane has been successfully adopted.

The most extensively used technology for producing polymeric membranes is non-solvent induced phase inversion. Phase inversion is a demixing method in which a previously homogeneous polymer solution is altered in a controlled manner. Loeb and Sourirajan pioneered the phase inversion procedure in membrane technology in the 1960s, and it is the foundation for most commercially available membrane synthesis. Phase inversion is a demixing method that transforms an initially homogeneous polymer solution from a liquid to a solid state in a controlled manner.

Figure 3 Schematics of non-solvent induced phase inversion method used for preparation of porous membrane.

The polymer solution is created in a suitable solvent or a mixture of a volatile non-solvent, and the solvent is allowed to evaporate, resulting in coagulation bath precipitation as shown in Figure 3. The solution system's core components are polymer and solvent, but various additives can be added to adjust the membrane's porosity, pore dimension, and overall morphology. Nonetheless, when producing the casting solution, the choice of polymer is critical. The solvent, in which the polymer must be soluble in an acceptable concentration, is the next critical parameter to optimize, since it is directly related to the final membrane application. Once the polymer is dissolved, the homogeneous polymer dope solution is cast on the glass plat for free standing membrane

and on support porous layer or fabric for composite membrane with the help of doctor's blade or suitable spreading rods. The rods are then stretched apart to achieve consistency throughout the film. Then as cast thin polymer film with/without support will be immersed in gelling bath covering non-solvent (miscible with solvent) to facilitate solvent and non-solvent exchange in polymer matrix. The polymer film starts precipitating out upon solvent/non-solvent exchange, into a porous precipitate membrane within the coagulation bath. The miscibility of solvent and non-solvent interchange within the coagulation bath, results in demixing and precipitation immersion, separating the two phases of polymer solution to polymer-rich and polymer-poor phase. During the phase inversion process, a thermodynamically stable polymer solution is tending to change from liquid to solid state in a controlled manner. Here, the solvent, non-solvent, solvent evaporation and coagulation period determines the structure, size and shape of the membrane pores. Further, as formed membrane can be heat treated to facilitate optimal mechanical and chemical strength to resulted membrane.

In some cases, the transfer of the fragile, ultrathin film onto the microporous support is the method's principal drawback. Thin film is typically transported by sliding the support membrane under the spread film. With extra care taken, the small segments of membrane as thin as 1 to 2 μm can be easily transferred with this approach. On the other hand, thin film of polymer can be directly coated microporous hygienic, defect-free and very excellently microporous support. In all composite thin-film membrane preparation procedures obtaining defect-free films involves substantial attention to set optimization parameters. In all supported membrane preparation procedures, the nature of the microporous support is critical and plays an important role in overall performance and shelf-life of a membrane [7,8].

Furthermore, by modulating various parameters, phase separation of a casting solution into a support polymer can indeed be efficiently controlled to obtain appropriate pore characteristics and morphologies as well as desirable sticky capabilities. These include the use of appropriate co-solvent and non-solvent combinations, controlled evaporation, thermal precipitation by adjusting both the solution and coagulation bath temperatures, and precipitation from the vapour phase by immersing the cast film in a non-solvent vapour phase. As a result, these variables are inextricably related to thermodynamic and kinetic factors. The viscosity of both the casting solution rises significantly as the polymer concentration in the solution increases. As an outcome, the system's period before precipitation gets larger, even though the period changes linearly rather than rapidly.[9] Natural skinned asymmetric crosslinked polyimide (PI) NF membranes suited for organic solvent nanofiltration (OSN) are made at industrial scale using this

technology. The preparation of polymer-based hollow fibre membranes involves similar techniques and parameters, apart from module design [10].

4.2 Thermally induced phase inversion technique

Thermally induced phase inversion was first proposed and researched in the 1980s to fabricate microporous membranes, but it received scant attention since NIPS was considered to become a more convenient and adaptable way of creating polymeric membranes. TIPS study is currently gaining popularity recently, leading to the advent of membrane contactors, that offer a number of distinct advantages, including process simplicity, high reproducibility, and a low tendency to form defects, as well as high porosity and the ability to create interesting microstructures with a narrow pore size distribution. Therefore, parameters can be optimized to achieve membrane reproducibility by controlling polymer reassembling during thermally induced evaporation. TIPS emphasizes polymorphism utilizing solvents and process parameters as a distinguishing aspect. Figure 4 illustrates the overall procedure for generating porous membranes using the TIPS approach [11].

Figure 4 Schematics of porous membrane preparation procedure via Thermally Induced Phase Inversion Technique (TIPS) method.

The TIPS process includes the following steps: 1) Is to dissolve a polymer vigorously in a high-boiling, low-MW solvent at an elevated temperature, typically around or above the

polymer's melting point to form a homogeneous melt-blend. 2) Forming the dope polymer solution into the desired shape and size on a suitable substrate, such as with a glass plate for a free-standing flat sheet, a porous support for a composite membrane, or hollow fibres. 3) To cool the cast solution to induce phase separation and polymer precipitation, and 4) To separate the diluent, generally by solvent extraction, to yield a membrane. Hence, Phase inversion is a precise balance of polymer–solvent interaction, cooling rate, chilling media, and temperature gradient.

One of the TIPS method's distinctive qualities is the ability to build membranes from semi-crystalline polymers that may not be ordinarily soluble in solvents at higher temperatures, as previously discussed. TIPS is regaining popularity as a viable platform for fabricating highly porous microporous membranes. There has been intense research in membrane technology for more sustainable techniques to produce polymeric membranes employing green solvents. To achieve long-term goals, green solvents with high volatility have recently become popular, making the TIPS approach more economically friendly. PVDF-type polymers have shown great promise in the development of microporous membranes [12,13].

5. Membrane separation process spectrum

Polymer-based membranes find several applications because the polymer offers flexibility in membrane design and module adaptation. This makes membrane technology a cost effective, a high pre-concentration factor with a large degree of selectivity and ease of operation [14]. Polymer-based membranes have a wide range of applications due to the ease of the polymer in membrane design and module adaptability. Membrane technology is therefore cost-effective, convenient to use, and also has a high pre-concentration factor with a high degree of selectivity. Membrane separation processes offer a range of membranes, as shown in the Figure 5, that mainly depends on the size and nature of the pollutant to be treated. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse or forward osmosis (R-O), and ion-exchange membrane processes such as Electrodialysis are examples of these [15]. Membrane separation is a wide term that refers to the process of deciding the quantity and specific pollutant rejection potentials of a membrane. The pressure required to remove the pollutants from the mixture/feed is used to classify the membrane process spectrum. Microfiltration membranes have the highest pore size and are used to filter out big particles and microorganisms at low pressure. Ultrafiltration membranes contain smaller pores than microfiltration membranes, so they can reject bacteria and soluble macromolecules like proteins at slightly higher pressures in addition to large particles and pathogens [16]. Nanofiltration is a relatively novel membrane category which fits between dense membrane and

ultrafiltration pore regimes and operates at a moderately high pressure. Nanofiltration membranes are hence referred to as 'loose' reverse osmosis membranes. Nanofiltration membranes are porous membranes that are often manufactured in an asymmetric manner. As a result, NF are porous membranes with pore sizes of ten angstroms or less that function somewhere between reverse osmosis and ultrafiltration membranes. With pore sizes of less than 1 nm, reverse osmosis membranes are effectively non-porous [17, 18].

5.1 Microfiltration

Microfiltration refers to the membranes category where pore size actively range in the 1 μm to 10 μm . This regime requires minimum operating pressure to generate permeate fluxes. Separation from MF is based largely on molecular separation, and yet process conditions could have a direct effect on the separation efficiency [19]. MF is used for numerous process applications such as dairy product separation where is defatted in the manufacturing of whey protein isolates, casein and serum proteins are separated from skim milk, and cheese brines are clarified. The MF membranes are made using polyvinylidene fluoride (PVDF) polymers, poly(ether sulfone) and polyacrylonitrile. The other common applications of MF membranes was found in sugar and sweetener, and industrial bioprocessing industries [20]. MF is used to purify fermentation liquors prior to further refining operations in this scenario. MF is frequently used in the industrial bioprocessing industry to clear bulk fermentation streams and increase the performance of downstream processing stages. The MF process is utilized as a pre-treatment step for other separation processes such as NF and RO in a variety of applications.

Figure 5 Infographics of membrane separation processes with pore size and separation spectrum.

5.2 Ultrafiltration

The ultrafiltration materials are made from a pore range of from 0.01 to 0.1 μ m in pores and further classified by Daltons (Da) or kilo-Dalton based on their molecular weight-cut-off efficiencies (MWCO) (kD). Typically, MWCOs of UF membranes range between 1,000 Da (1kD) and 100,000 Da (100kD). Like MF, the separation regime of the ultrafiltration process depends mainly on molecular exclusion, but process conditions, such as applied pressure, depend on the type and distribution of the pore [21]. MWCO membrane, on the other hand, can be tuned again for final application. Polyvinylidene fluoride (PVDF), polyethersulfone (PES) or polysulfone (PS) polymers are the most widespread used polymers for UF applications. In RO and NF thin film composite (TFC) membrane applications, the substantial majority of PS-based UF membranes are used as a supporting membrane [22, 23]. Much farther specific utilization of UF membranes would include UF membranes for the dairy processing, pain industry, resin recovery, bioprocessing industries, domestic wastewater treatment, industrial wastewater treatment, process water recovery and macromolecular augmentation. [24].

5.3 Nanofiltration

Relatively new addition to the membrane separation spectrum is the nanofiltration (NF) process. Tight ultrafiltration regimes have been made reference to as the industrial reference to NF. Magnesium sulphate (MgSO_4) and sodium chloride are the main features of NF membranes that are based on their rejection characters (NaCl). The rejected range is generally projected to be ~ 90 - 99.5% and ~ 300 - 70% , respectively, for MgSO_4 and NaCl for NF. The separation mechanism of NF is based in large part on diffusion by the membrane of dissolved species, and pH and chemical loads can be severely affected near or on the surface of the membrane [25]. Recently, the most common use of NF is the demineralization of industrial process intermediaries, as an alternative to both UF and MF processes, combined with concentrating macromolecules. The NF process has evolved over the years as an important separation process for applications such as molecular separation, demineralization, desalination, organic weight loss and waste water treatment. NF is used for removing impurities and enriching primary sweetening components in sugar and sweetener industries [26].

5.4 Reverse osmosis and forward osmosis

The Reverse Osmosis (RO), which categorises the separation range based on rejections features of conventionally sodium chloride, is a commercially most popular membrane in

separation ranges. The NaCl range is expected to reach ~96-99.8% for RO membranes. As with NF, the separation with RO is based largely on the spread of dissolved species by the membrane and the osmotic pressure of the process fluid or feed [27]. The RO membranes are generally prepared with the selective thin layer and support for ultrafiltration in thin-film morphology. The thin layer of polyamide is commonly used on the ultrafiltration support of polysulfones. The RO is widely used after UF or NF as an effective tool for various applications for molecular separation, desalination and treatment of wastewater. The use of RO process in-house has revolutionized recent developments in nanotechnology innovation, modified RO composite membranes. Household RO applications also forced its use of RO modules in miniature with greater separation efficiencies in innovative ways [28].

6. Material choice for polymer based membranes

The selection of an appropriate polymeric materials is a key component of effective, physical and chemical separation membranes. Polymer nature and the membrane process play an important role in obtaining the resulting membrane's enhanced permeability, selectivity and durability. Polymeric membranes, also known as organic membranes, include a family of technology for liquid separation which is industry leader in efficiency and performance. These membranes are generally recognized in four main categories based on efficiency and separation characteristics. An earlier discussion (microfiltration, ultrafiltration, nanofiltration and RO). The polymers utilized in the fabrication of each membrane classes are carefully selected to ensure excellent performance in a specific process environment. Compatibility must be taken into account with the fluid(s) to be processed and cleaning materials required to help maintain hygiene and stability in performance. Polymers include polysulfone/PS/PS, polypiperazine and polyamide, as well as polyvinyl fluoride (pvdf) [25]. Further, list of some of the synthetic polymers used for various type of membranes have been recorded in Table 1.

6.1 Synthetic polymer membranes

Roughly every commercially successful membrane consists of organic synthetic polymers such as polysulfones, sulfone polyether, poly(vinyl diameters), polyacrylonitriles, cellulose acetate, and so forth. Microfiltration, ultrafiltration with large pores and different solution preparation conditions with adopted parameters frequently consist of identical polymer materials. During membrane preparation process coagulation, pore size control will usually be followed to produce various pores and morphologies.

Table 1 List of some of the synthetic polymers and their structures used in membrane preparation.

No	Synthetic Polymer	Structure	Ref.	No	Polymer	Structure	Ref.
1	Polysulfone (PSF)		[29]	7	Polyvinyl alcohol (PVA)		[30]
2	Polyvinylidene fluoride (PVDF)		[31]	8	Polycarbonate (PC)		[32]
3	polyether sulfone (PES)		[33]	9	Polyurethane (PU)		[34]
4	Polyamide (PA)		[35]	10	Polyimide (PI)		[36]
5	Cellulose acetate (CA)		[37]	11	Polyvinylpyrrolidone (PVP)		[38]
6	Polyacrylonitrile (PAN)		[39]	12	PIM-1		[40]

Materials from inorganic materials such as ceramics or metal oxides/hydroxides can also be prepared with composite membranes of polymer origin. Further, blending composite membranes seems to be possible to achieve porosity and permeability ranging from microfiltration, ultrafiltration or nanofiltration. In terms of thermally stable, chemical resistant, composite membranes have proven to be an advantage over only polymer membranes. On the other hand, there are also several downsides with ceramic membranes processed for implementation in microfiltration, such as a high cost and mechanical fragility that prevented their widespread use. Likewise, metallic membranes often consist

of stainless steel and can be porous very finely. It is mainly used for gas separation, but may also be used as a membrane support or for water filtration at high temps. However, for large-scale use, metallic membranes pose difficult issues in design and module preparation and pose several logistical problems. The current tendency on membrane development is to use Nano-functionalized membranes. Polymer membranes with active nanoparticles besides bio foliation avoidance are an example of modern membranes that are becoming extremely important because of various proven advantages over polymer membranes alone.

Furthermore, synthetic membranes can be classified as organic and inorganic. Inorganic membranes include various materials, such as zirconia, alumina, titanium, palladium and silver, for example, ceramic, carbon, zeolites and oxides of metals. Organic membranes, like polytetrafluoroethylene, polystyrene and Polyamide and others that form macromolecules, are used for the majority of commodities and industry [41]. In order to achieve increased properties, enhanced film strength and cost effective maintenance of the conventional scale-up protocols, use these synthetic polymers to prepare blends for use as membranes [42, 43]. Inorganic synthetic membranes, even so, seem to be hugely reliant on the mechanism of charge exclusion to promote electrical refusal and mass transport. Charging properties can be easily adjusted in the membrane surface, however, to ensure optimum pollutant refuse and separation performance through different parameters, like feed solution pH and ionic strength conditions. When the optimum load on the surfaces of the pottery membrane is changed, the overlap effect of the double layer will avoid the ionic rejecting patter as distance potential attenuation is seldom assessed to determine the extent of this possible overlap [44,45]. The main advantages of the synthetic polymer membrane are that polymers offer extensive opportunities to change in the form of composites and blends and can also be customized to make them adaptable in any form, such as flat sheet and hollow fibre [46]. Over the years, progress in the science of polymers has permitted a variety of innovative polymers available for membranes with special features that can be used through various morphologies in particular.

6.2 Biopolymer membranes

Table 2 List of some of the important biopolymers used for membrane application.

N o	Biopoly mers	Structure	Ref.		Biopolyme r	Structure	Ref.
1	Chitosan (CS)		[47]	8	Poly(lactic Acid (PLA)		[48]
2	Sodium alginate (SA)		[49]	9	Polyhydrox yalkanoate s (PHAs)		[50]
3	Agar (AG)		[51]	10	<i>Polyhydrox ybutyrate (PHB)</i>		[52]
4	Agarose (AGR)		[53]	11	Pullulan		[54]
5	Chitin (C)		[55]	12	Nitrocellul ose (NC)		[56]
6	Cellulose		[57]	13	Cellulose acetate (CA)		[58]
7	Carragee nan (CAR)		[59]	14	Cellulose triacetate (CTA)		[60]

For numerous material and process applications, biopolymers include a variety of naturally occurring polymers (Table 2) from renewable resources. Biomacromolecules or biopolymers are generally known as substances produced through live organisms. Their unique characteristics and abundance have recently been taken into account in the research and development of sustainable end products. Biopolymers are chain-like molecules composed of repeated chemical blocks, which easily deplete biomass

resources in the environment. Many repeat units are active in several product segments today with cellulosic products and their biopolymers derivative. On the other hand, plenty of others continue to stay uncovered and underutilized. Biopolymers have opened up to greater utilization in membrane applications with a rapid development of the understanding of basic biosynthetic pathways and bioprocessing protocols. A range of polysaccharides, proteins, lipids, polyphenols and specialty polymers are derived from the biopolymer backbones. The use of these sections will also help to glue and manage final products. Many other synthetic and biopolymers with an increased interest in green and durable materials are being modified to suit biopolymers. This would add value to environmental compatibility and enhance protection [61]. Also, hydrophilic and biocidal properties of biopolymer membranes with unique wettability have drawn considerable research interests for addressing challenges biocompatibility and biodegradability [62]. Several advancements in thin film and even in the scientific fields of functionality have also led to the remedy of new membranes in conventional membranes, such as fouling, scaling and biofouling. The durability of a membrane was increased, but the maintenance and operating costs were also drastically reduced when used. Building on these reasons, membrane processes are an intensified process that offers a number of advantages, including lower energy and reduced plant volume, as expected by the process intensification strategy.

Biopolymers which have properties along with biocompatibility, biodegradability, portability and ecological responsibility can therefore be a legitimate alternative to the conventional polymers based on petroleum. Biopolymers have shown great potential for water treatment and wastewater treatment, as biopolymers could be used to modify their physical and chemical properties such as pH, temperature, mechanical and thermal stress, etc. [63]. Moreover, biopolymers display low toxicity for human health, high biocompatibility and biodegradability [64]. In large-scale membrane production, various biopolymers such as CA, CS, PLA, PHA, PHB, TPS, PVA and PU are now substituting conventional polymers such as PSF, PES, PI etc. The other important property of biopolymer is that the majority of biopolymers are inherently film-forming and have a high affinity for water and a composite potential for different nanomaterials. However, there remain significant drawbacks in membranes prepared with biopolymers such as low mechanical strength. Nevertheless, biopolymer membranes with enhanced mechanical characteristics have been produced using nanomaterials which can potentially be of immediate prosperity.

6.3 Membrane modules and types of modules

Once Membrane is prepared in large scale, adopting the as prepared either flat sheet or hollow fibre membrane in to engineering module becomes crucial to extract optimal performance from the device. Engineering the membrane into module form is art of extracting maximum from the membrane itself. In the past several innovative pathways have been seen in the way the membrane is converted into engineering devices and components to separate the feed into permeated and resentful streams. Based on their structure and arrangements, commercially successful modules are therefore classified, and the industry uses four different kinds of membrane modules. They are (1) Flat sheet plate and frame modules, (2) Spiral-wound modules, (3) Hollow fibre modules, and (4) Tubular modules.

6.4 Plate and frame module

Figure 6 Schematic and actual membrane module and plant prepared using flat sheet membranes.

Yet another platform and frame module are designed in a metal frame with flat sheet membranes and spacers, as shown in Figure 6. Depending on the relation between two solutions, the model also shows three possible modes of plate and frame module. These three modes may work in the same operating conditions differently. Four conditions are employed to simulate the plate and frame module: the volumetric flow of the feed and solution drawing, the concentration of the drawing solution, the flow direction and membrane orientation. The flat and frame module is the simplest device for packaging flat sheet membranes among all membrane modules [65]. Plattened-and-frame modules, like stripes, size and shape of research lab devices holding a single, small membrane,

systems with membrane series that can be used to contain plate and frame modules, are designed and developed in various directions. In the plate- and frame module, between two geometric types, the horizontal rectangle and vertical rectangle are designed for feed flow in the cross-current flow direction. A single membrane sheet with a lower pack density is simulated in the plate and frame module [66]. However, this module is easy to operate and handle among all membrane engineering modules for large-scale panel and frame module in industrial applications.

6.5 Spiral wound module

Most commonly used spiral injury modules and successful, commercial membrane modules exist in the membrane market due to their high volume-to-membrane surface. Spiral membrane module consumes an enormous amount of other than membrane engineering material itself. A spiral-wound module has the membrane, the feed and the permeate channels, the membrane spacing, the permeate tube and the membrane housing as the main components. This module strategically places engineering materials such as feed and permeate distances to avoid feeding or permeate fasteners in separation experiments. Although the channel spacer may increase mass transfer near the membrane, the pressure loss along the membrane leaf inevitably increases as shown in Figure 7. During the spiral membrane wound process membrane sheets are glued to form an envelope on three sides with spacers and support layers. More envelopes are attached and rolled up around this permeated tube in order to create feed channels and permeate. The membrane sheets are positioned in a pressure-module containing membrane packaged in a sticked or plastic thread, which stabilises the assembly once it has been finished. Used three or more modules in series are usually connected to a pressure vessel for optimal output. The performance of the modules is influenced by many factors in the spiral wound membrane: 1) propensity and capability to foul; 2) quality control and operating conditions, such as feed pre-treatment, feed concentration, food supply pressures, and permeate recovery, 3) distances that have a large impact on the locally mixed, mass transmission, and the extent that concentration polarization and pressure loss are determined [67,68]. Spiral wound membranes are widely used to remove calcium and other divalent ions from hard drinking water in under-the-sink nanofiltration modules. Many modules in the industrial scale include membrane envelopes wrapped around the central collection pipe, each of which has an area of 1-2 m².

Figure 7 An overview of the spiral wound membrane from schematics to end product.

The design is straightforward when the membrane is wrapped between spacers and supports, consisting of a membrane envelope of spacer and membrane wound around a perforated central collecting tube. Finally, all this spiral wound is placed within a tubular pressure vessel around the collection tube. Feed goes through the membrane envelope axially through the module. One part of the feed penetrates the membrane envelope, spiralling to the centre and exiting through the tube. Nanofiltration and ultrafiltration spiral-wound modules have been applied extensively for applications of reverse osmosis in the desalination, organic molecular separation, and food processing industries

6.3 Hollow fibre module

Figure 8 Actual photographs of bundle of hollow fibre membrane, their spinning process, ready to use module and schematics of separation mechanism in hollow fibre modules

The hollow fibre membrane segment (HFM) encompasses more than 50% of the membrane markets used in water treatment as this sector has superior packing density, higher volume surface and self-supporting capacity in the membrane module form. Hollow fibre membranes are an artificial membrane class with HF that acts as a semi-permeable bundling barrier with no other material that enables the use of economically cost-effective engineering. The HFMs have a porous, separating layer coated polymer fibre structure. The polymer density increases in order toward the outer surface of the fibre or vice-versa, depending on the direction to which it flows [69]. This design is easy to make and makes it necessary to contain very large membrane areas within a cost-effective system. Hollow fibre membrane with little diameter can withstand operating conditions in packaged conditions to prevent collapse of the fibre in high applied pressure. Typically, the internal diameters and thick walls of HFM are 50 μm and the outer ones are 100 – 200 μm . HFMs are becoming more popular because of their high packaging density, mechanical stability and high permeate output compared with all other membrane modules. Contactors with a wall thickness of <1 mm and a pore size <0 have high specific contact surfaces (m^2/m^3), <1 mm internal diameter. and pore size <0.3 microns, a tube in shell configuration is used as shown in Figure 8. HFMs are also known

for their physically robustness, prerequisite limited space for use, and simple housing engineering protects the delicate hollow fibre membranes [70].

In their mechanistic separation, hollow fibre membranes are also classified into two types, i.e. 1) inward to outer and 2) outer to inland which indicate feed flow and permeate direction. Types of HFMs are also classified in three types for membrane preparation (doping and polymer solidification) methods. 1) Spinning of the melt: The Polymer is directly heated by melting in an inert atmosphere in a chamber above its melting point and the melting polymer is extruded by a spinneret. As soon as the melt polymer is crossed, the cooling immediately leads to a transition to the phase and solidifies the polymer. This produces a capillary or HFM with a uniform structure. 2) Dry spinning: The Polymer is dissolved in a highly volatile solvent by the dry spinning technique and the solution is extruded by a known spinneret diameter. The polymer solution is heated during extrusion and, due to solvent evaporation, the polymer solidifies which lead to the development of HFM, and 3) Wet spinning: the extruded polymer solution will be immersed in a non-solvent bath during this process. There is an air gap between Spinneret and non-solvent Bath, where membrane formation begins with a particular thickness of the inner wall [71].

6.6 Tubular membranes (ceramic membranes)

Self-supporting membranes are not tubular membranes. They are located within a tube, generally of inorganic materials, made of a special kind of material. In most of the tubular packages, the membrane inside is supported and housed. Ceramics and their composites are the most popular membrane material used in the tube membrane module. These materials are fragile and at times breakable, so that tubular membranes are placed inside the tube, the tubular membrane flow is normally inside a tube. Due to its excellent mechanical stability, chemical and thermal resistivity, ceramic membrane has attracted considerable concern and are cost efficient for some extreme applications where polymeric membranes are not easily maintained. Ceramic membrane has the advantage of its thermal and mechanical properties that make it possible to sinter at a much lower temperature than alumina. Although several studies have demonstrated the benefit of the ceramic membrane, sustainable developments in ceramic membranes have hindered the use of them because of their non-flexible and fragile nature.

Figure 9 Structure and morphologies of multi-channel alumina-based ceramic membranes.

Ceramic containers, nevertheless, are less expensive, effective and higher performance compared to polymers, applied in extreme conditions such as pH-like, high temperature and harsh solvent conditions [72]. For the removal of suspended matter from the ultrafiltration and microfiltration range ceramic membranes are effectively used. Ceramic membranes are usually made from oxides of aluminium, titanium or silicone that are stable under extreme feeding conditions. The advantages of ceramic membranes are that they are chemically inert and stable at high temperatures in which the polymers are ineffective. These physical and chemical properties make ceramic MF/UF membranes particularly suitable for food, cooling power stations, highly contaminated treatment of waste water, biotechnology and the pharmaceutical industry in which membranes require repeated sterilisation and cleaning of steam by aggressive solutions. These pores are in the pack of different sizes of nanoparticles of a metal oxide at high temperature and pressure as illustrated in Figure 9 and range from 0.01 to 10 mm in ceramic membranes for a microfiltration and ultrafiltration range. In general, these membranes are produced through a slip-coating and sole-gel extrusion process. Other techniques, especially sol

gel-powered techniques are used for the fabrication of pores between 0.001 and 0.01, as well as for the manufacture of highly packaged small ceramic pores prepared via soil-gel methods, are suitable for use in gas separation [73]. The traditional method of preparing ceramic membranes is through a multistep process of manufacturing using powder composites of ceramic or metal oxide, which depends on the application and membrane configuration following shaping, heat processing and layer deposition procedures [74].

7. Advanced polymer membranes

7.1 Block copolymer membranes

Controverted structure requirements for advanced antifouling membrane for a range of applications such as CO₂ capture, seawater desalination and other industrial applications require new approaches to membrane science and membrane manufacture. Limitation of pore size and distribution is the main disadvantage with conventional membrane preparation. The molecular manipulation of a porous structure in combination with surface chemistry is now a well-known approach to the creation of emerging physical pores to increase the features of all membranes in certain application applications using a block copolymer self-assembly route [75]. Block copolymers pave the way to overcome the disadvantages of the conventional membranes. These polymers can be used either as porous or pore films, hollow fibres and particles. As the main advantage of the block copolymers for membrane manufacture, this polymer is multi-purpose morphology which can be controlled by adjusting the chemical composition and the length of the block for the desired porous dimensions. With a self-assembled block copolymer route different chemical structures can be obtained in just one polymer and selective dense layers with a particular porosity and composition can be prepared in combination with other nanocomposite materials that find huge applications in gas separation, pervaporation, nanofiltration and fuel cells [76, 77]. Besides its self-assembly property, diblocks and triblocks are equipped with micro-domain isolation, which shows an amazingly complex and periodic geometry which has unlimited nanoscale engineering potential for porous membrane applications [78]. The self-assembly di-block copolymers produce the selective deterioration of one-block spheres, lamellae, cylinders and complex nanobicontinuous pores. The copolymers of triblock, on the other hand, produce more complex structures with numerous morphological components unknown to science and technology membrane community but that could revolutionize the properties of fluid transport [79]. The first block copolymer membranes was reported half a century ago as charge-mosaic membranes [75]. The whole charge murals are the arrays of loaded domains containing paths for both anions and cations, both anion-exchange and cation-exchange. The first copolymer cast on substrate to achieve its purpose was poly(styrene-

b-2-vinylpyridine. In 1975, Odani et.al in addition, in order to create an ordered porous structure, used poly(Styrene-butadiene-styrene) (PSBS). Authors followed two important approaches in this method to pore production: 1) film casting-selective block sacrifice and 2) self-assembly through non-solvent-induced phase separation (NIPS). In applications such as gas separation, ultrafiltration, nanofiltration, pervaporation, fuel cells and batteries, copolymer membranes produced through the method have been used. Recent developments have shown a promising self-assembled copolymers with PEG and fluoro-blocks as innovative insights for proposed anti-fouling applications [80]. On the other hand, oligomerically polymerized polyamide membranes with successful integration of anti-fouling properties have been recently incorporated into oligomeric zwitterionic building blocks [81].

7.2 Functional polymers-based membranes

Functional membranes offer multiple features, both help in the separating pollutants or contaminants from an aqueous solution and also contribute to adsorbing, degrading and/or disabling contaminants. Functional membranes based on polymers are generally designed and adapted to specific applications. These membranes are used to filter out organic and inorganic contaminants like dyes, emerging pollutants, and heavy metals, etc. [82]. The production of membrane using functional polymer involves processing polymers and the subsequent formation of membranes in which methods regularly followed have to be modified in order to achieve stable membranes [83]. This process maintains its original properties while providing new properties such as hydrophilicity, bio-compatibility, anti-static characteristics and performance. Nanomaterials such as clays and other colloidal suspension are also used to optimise the functionality of polymers to optimise different parameters relating to treatment such as adsorption properties, swelling patterns, and rheological/colloidal phenomenon.

7.3 FO membranes

Among other membrane separation processes, the FO process is recovering its momentum. With conventional pressurized techniques at molecular level the use of FO can be achieved with special application. Unlike the pressure-driven membrane processes, FO is an osmotically driven, low-hydraulically operated membrane process. In the absence of the applied pressure, the flow rate of FO was higher than that of the pressurized membrane processes, less membrane fouling and more energy-efficient [84]. As a matter of principle, FO is a spontaneous method where solvent permeates a FO membrane from a solution that has higher chemical water potential (feed solution) (draw solution) [85]. For years now, for FO-operations, RO-membranes have been used in combination with suitable recyclable pulled solutes as effective semimeter membrane

from CA, CTA, PA and the Composite polymer [86]. In absence of dedicated FO membrane, In recent years, molecular design of FO membranes with high flux and power density has gotten a lot of interest in research and development [87,88].

7.4 Polyelectrolytes complex membranes

Complex (PEC) polyelectrolyte systems have unique loading and surface properties to be used for separation and purification. PEC-based membranes have already shown promising materials, namely pervaporation and nanofiltration, for diverse membrane separations [89,90]. Polyelectrolyte have a strong tendency to adsorb on the surfaces of the particles in an aqueous suspension [91]. The groups of organic polymers charged are called polyelectrolytes when hydrolyzed and have many of their properties. They can be used to convey neutral particles with surface charge. Polyelectrolytes are cost-effective, quick, performance-efficient, thick and controlled. The method is also easy to use for the modification by composite membranes of commercially available membranes. In terms of molecular structure, weak and strong electrolyte activity, molecular weight and charge density the polyelectrolytes can be differentiated [92]. PECs are able to separate through different mechanisms because of the electrostatic repulsion forces. This kind of repulsion is also maintained in very open structures due to its high charging density. In water treatment applications, PECs can provide extreme thin, but effective barriers. With the incorporation of polyelectrolytes on the existing membrane surface, the development of membranes has been greatly improved. In most cases, polyelectrolyte charge can effectively be applied when the salt ion penetration is rejected via a polyelectrolyte-modified membrane [93]. Polyelectrolytes can also be used with a good control over the distribution of ionised molecules within the thin film in several other existing membrane surface modifications. Polyelectrolyte complex membranes can generally be made from a stock of biopolymers and are highly biocompatible, non-toxic and capable of film formation. PECs also offer promising methods to integrate multi-layer architecture with membranes and surface properties can be modified to adjust membrane load and hydrophilicity [94].

7.5 Polymer-based aerogel membranes

Aerogel are a special kind of functional material with ultra-porous solid gel, with a gas-inducing solid network structure that completely replaces the liquid part [95]. The Aerogel consists of a 3D network like a solid structure in the form of highly cross-linking structures that has a large number of air-filled pores. The 3D structures can be developed using different precursors as illustrated in Figure 10.

Polymer-driven aerogels are recently gaining attention because of their easy handling and their extensive potential for application [96,97]. Aerogels with two characteristics, structural properties and functional properties, can be distinguished from other porous materials. Structural characteristics consist of a gel-like structure of hierarchical, fractal and non-crystal microstructural structures, crosslinks, granules or powders. The characteristics of functionality resulting from structural properties are unique in terms of bulk characteristics such as hydrophilicity, high-spectrum, high porosity and a high mechanical resistance, low dielectric constant, low sound speed, high-density surface area and high-speed porosity [98].

Figure 10 Photographs of Aerogels made from different precursors (a-c) polymer aerogel from polymer gel to aerogel, and (d) Polymer-based nanocomposite aerogels.

8. Membranes for ground water treatment

The remediation of contaminated water gains the highest priority because of an increased water scarcity and water contamination, both at industrial scale and on groundwater resources. Thousands of people around the world are exposed to contaminated water sources such as heavy metal, active pharmaceutical ingredients, organic matter, and emerging pollutants. APIs are contaminated with pollutants [99]. For various types of contaminants with different chemical and anthropogenic sources, innovation is required in membrane technology. Long-term ingestion of heavily metal-contaminated water may be at risk of lung, bladder, kidney and skin damage and cancers according to the World Health Organization (WHO) [100]. Several technologies for heavy metals remediation and organic contaminated groundwater have revealed certain definite results such as: 1) full or substantial pollutant destruction and degradation initiating further investigations in

the nature of degraded components, 2) pollutant extraction for further processing or disposal, 3) stabilization in less moving forms of contaminants. Therefore, membrane technology can be used in conjunction with other means to rectify unsolved problems in purifying contaminated water sources [101].

9. Polymer membranes in energy conversion and storage devices

Figure 11 Structures of ion-exchange polymers popularly used in energy storage and conversion devices.

In this era of electronic devices, it is highly desirable to develop lightweight, flexible and folding electrodes and polyelectrolytic membrane with decent mechanical durability and

electrochemical activity. In this context, it is still an incredible challenge to find suited polymer-based membrane with suitable ion-exchange characteristics for electrochemical storage systems such as batteries and supercapacitors as well as conversion devices such as FCs. Among several polymers, freestanding robust PANI in the form of a leuchemeraldine base (LEB), emeraldine base (EB), pernigraniline-base (PNB), polypyrrole (PPy), polythiophene (PT), poly(p-phenylene) (PPP), polysulfone/poly (Ether sulfone) (PSf/PES), polyimide/poly(ether imide) (PVPEI) (Figure 11). In addition, most of the polymers can be converted into wearable solid state supercapacitors, high electrochemical performance batteries and fuel cell devices and decent mechanical durability. The lightweight, flexible and folding polymer-based ion exchange membrane represents both an electrode and solid electrolytic materials for electro-chemical energy storage systems of the next generation.

Conclusions and future perspectives

For years, PANI, PPy, and Nafion membranes have been an ion exchange membrane used for energy storage and conversion devices (individually perfluorinated polymer containing sulfone groups). However, in almost every sector of the economy, bio-origin functional materials and polymers emerge as potential materials for various and diverse purposes. Researchers have recently spent considerable time finding the right combination of natural materials for sustainable energy applications. Important applications for energy storage and conversion are now developing as nanoscience and materials processing technologies develop. Volcanic eruptions and rock weathering could produce natural polymers and functional materials, while anthropogenic sources could be obtained by the release of non-refined waste, biomass and algae sources. Recent developments in the field of biomaterial-based polymers have shown efficient utilisation in preparation of an electrodialytic membrane, fluid membrane, nanofibre-like separation membranes, etc.

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