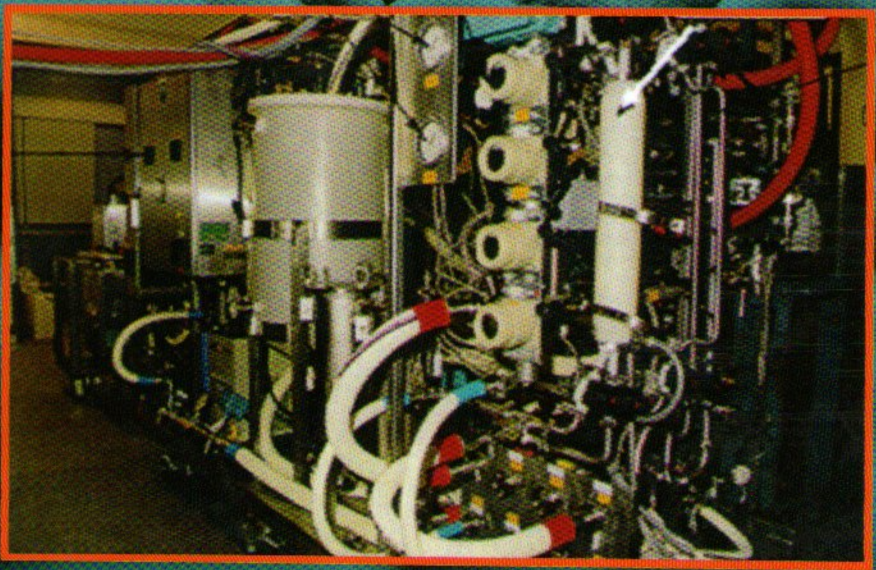
SECOND EDITION

Handbook of Membrane Separations

Chemical, Pharmaceutical, Food, and Biotechnological Applications



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Advanced materials for utrafiltration and nanofiltrationmembranes

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CONTENTS

1. INTRODUCTION TO MEMBRANE-BASED LIQUID SEPARATION PROCESSES

Membrane separation technologies refer to any separation processes in which membrane function as both a barrier and a sieve for separating feed species such as liquid mixtures and colloidal particle mixtures [1-3]. Compared with conventional separation methods, membrane separation technologies have the following advantages, (i) *Efficient*, Generally, a membrane separates feed species in combination of sieving effect and affinity effect. The development in material science helps readily the membrane separation of most difficult mixtures; (ii) *Energy saving and environment protective*, Size-based separation processes such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis(RO), involve without heat induced phase transition and require much energy loss consumption. Moreover, a considerable portion of membrane separation technologies play important roles in environmental issues such as water treatment, pollutant processing, and hazardous organics recovery; (iii) *Versatile*, the application scope of memebrane separation technologies is broad and flexible, benefiting both the industry and daily lives.

Membrane science can arbitrarily be divided into seven intimately related categories: material selection, material characterization and evaluation, membrane preparation, membrane characterization and evaluation, transport phenomena, membrane module design, and process performance. Among these categories, membrane materials are currently the most important part in membrane technology and it was experiencing significant growth. These materials differ in their performance characteristics including mechanical strength, fouling resistance, hydrophobicity, hydrophilicity, and chemical tolerance.Moreover, materials capable of performing multiple functions simultaneously or sequentially in time are of significance to improve performance of membranes.

For water treatment, hydrophobicity and hydrophilicity play very important role. Hydrophilic means water-loving and such materials readily adsorb water. The surface chemistry allows these materials to be wetted forming a water film or coating on their surface. Hydrophobic means water-hating and this materials has little or no tendency to adsorb water. Water tends to bead on hydrophobic surfaces into discrete droplets. The hydrophilic and hydrophobic properties of a membrane material are related to the surface tension of the material. The fundamental importance of the surface tension comparison is that liquids having lower surface tension values will generally spread on materials of higher surface tension values. Table 1 summarizes surface tension values of some polymeric membrane materials. It has been noted that the higher of surface tension value of material, the more hydrophilic the material is.

Table 1.
Summarized surface tension of some polymeric materials [4].

Polymer materials	Surface tension (dynes/cm)
Polytetrafluoroethylene	18
Polyvinylidene fluoride	25
Polypropylene	29
Poly vinyl chloride	39
Polysulfone	41
Polycarbonate	42
Polyacrylonitrile	44
Cellulose	44

Hydrophilic membranes tend to exhibit greater fouling resistance than hydrophobic membranes. Particles that foul in aqueous media tend to be hydrophobic. Hydrophobic particles tend to cluster or group together to form colloidal particles because this lowers the interfacial free energy (surface tension) due to the surface area exposure. To prevent fouling in water or wastewater treatment, a membrane requires a surface chemistry, which prefers binding to water over the other materials.

2. RECENT DEVELOPMENT IN MEMBRANE MATERIALS

Significant progress has been made during recent years in the development of new membranes and their applications. This development of a certain membrane process or application can be classified according to the driving force used in the process. The technically and commercially most relevant processes are pressure-driven processess, such as reverse osmosis, ultrafiltration and nanofiltration. In this chapter the principles of relevant membrane materials are briefly reviewed. An assessment of the present and future membrane materials is given. The structure of the membrane-based industry and its stategies toward the application and market are slightly described. Recent developments of new or improved membranes are discussed and further research needs for a continuous growth of membrane technology are pointed out.

Membrane materials are core parts of any membrane-based technologies [5-7]. In the past decades, the conception of multi-component or composite membrane materials has been a successfull methodology for designing membrane materials with optimum performances. This is because single component materials, no matter natural or synthetized, can hardly fulfill all of the requirements for making an idea separation membrane. On the other hand, multi component composite materials can combine advantages of different components and achieve optimum properties and performances.

Numerous interesting scientific and technological challenges are presented by the area of polymer-based membrane materials which are used for materials separation and catalysis [8-11]. The balance between the permeability and flux of a membrane material with respect to specific compositions of the liquids to be separated in specific applications with substantial market potential, such as drinking water process, require an extremely high degree of optimization, which is frequently not attainable with traditional homopolymers. For this reason, multicomponent polymers are also being developed. There is little known to date concerning the relationships between the topologies and properties of these polymers.The stabilization of the structure of polymers with intrinsic microporosity, which could be used for applications in the field of water separation, and also demonstrate particularly interesting properties in the separation of liquid material mixtures, offers another challenge.

2.1 ULTRAFILTRATION

Ultrafiltration (UF) has become one of the best alternatives replacing conventional liquid separation process. However, membrane fouling is a critical issue in UF process and also an important factor, which restrict its widespread application. Development of new materials is accompanied by developments in process engineering aimed at optimizing the design of separation processes.

The activities in this area are divided into two groups: polymer multicomponent and organic-inorganic hybrid materials. Due to the distinct advantages such as temperature and wear resistance, well defined stable pore structure, and chemical inertness, the inorganic membranes such as ceramic and carbon membranes are quite suitable for the processes involving high temperatures and harsh chemical environments and have been successfully applied to the water or wastewater treatment [12-14]. However, inorganic membranes display some inherent disadvantages and majority of them are related to their relatively high cost arising from the expensive materials, the complicated fabrication procedure and the low membrane surface [15]. Hence, the cheap and easy-fabricating polymeric membranes are still dominating the membrane market. It should be pointed out that the serious membrane fouling caused by nonspecific adsorption and/or deposition of foulant onto membrane surfaces, often results in a substantial decline of the permeate flux with operation time and consequently limits their wide application in the water and wastewater treatment [16]. Many investigations have demonstrated that modifying membrane surface, such as hydrophilicity, pore size, porosity and surface charge effectively inhibited the nonspecific adsorption and consequently decreases membrane fouling and increases significantly the permeate flux [17-19]. The improvement of polymer/polymer and poymer/inorganic blend membranes are most interesting, owing to its convenient operation under mild conditions and good performances of the resulting membranes.

2.1.1 Polymer/Polymer Blend Membranes (Polymer Multicomponent Systems)

The molecular self-organization of block copolymers with different topologies presents a remarkably fascinating strategy for the formation of nanostructured membrane materials. Molecular self-organization is the spontaneous arrangement of molecules in highly-ordered structures held together by intermolecular bonds. Although synthetic membranes are much more simply structured and demonstrate much lower degrees of functionality than biological membranes, their mechanisms of structural formation are nonetheless very similar. To this end, tailor-made block copolymers of differing chemical composition are synthesized, using controlled polymerization processes, and morphologically characterized. During this process, additional functionality can be provided by integrating stimuli-sensitive blocks, which results in switchable membranes. The process of structural formation during membrane production also plays a substantial role here. Also studied, in addition to pure block copolymers, are mixtures of various polymers, which are normally available commercially.

2.1.1.1 Integral-asymmetrical block copolymer membrane

The molecular self-organization of block copolymers with different topologies presents a remarkably fascinating strategy for the formation of nanostructured membrane materials, as shown in Figure 1 [20]. Molecular self-organization is the spontaneous arrangement of molecules in highly-ordered structures held together by intermolecular bonds. Although synthetic membranes are much more simply structured and demonstrate much lower degrees of functionality than biological membranes, their mechanisms of structural formation are nonetheless very similar.

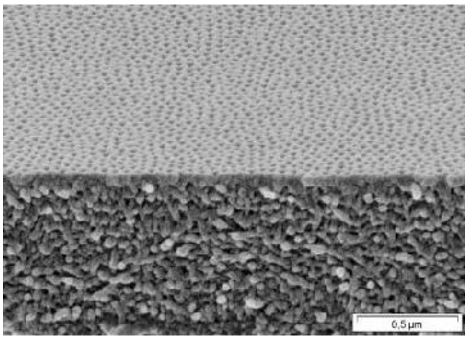


FIGURE 1 Integral-asymmetrical block copolymer membrane

To this end, tailor-made block copolymers of differing chemical composition are synthesized, using controlled polymerization processes, and morphologically characterized. During this process, additional functionality can be provided by integrating stimuli-sensitive blocks, which results in switchable membranes. The process of structural formation during membrane production also plays a substantial role here.

Also studied, in addition to pure block copolymers, are mixtures of various polymers, which are normally available commercially. All these systems should incorporate at least one semipermeable component, while other insoluble and non-swellable components serve to stabilize the membrane.

Table 2
Polymer/polymer blended membranes

Polymer used	Method	Remark	Reference
PES/PVP	Diffusion induced phase separation with acrylonitrile-based copolymer		[21]
SPC/PVDF	Sulfonation of polycarbonate thus blended to PVDF	The blend of two different polymers showed the slow low flux declinations, low fouling due to electric exclusion.	[22]
PS/PMMA	Direct blended	The polar group in PS enhanced miscibility in blend containing PMMA	[23]
PVDF/PC	Direct blended using PMMA as compatibilizer	This membrane demonstrated that 40% of PMMA generates	[24]

		an increase in miscibility and a beneficial effect on permeability.	
PEI/SPEI	Direct blended	These SPEI/PEI membranes showed anti-fouling properties regarding BSA flux at pH 8, achieving 32% reduction as compared to 75% PEI.	[25]
PVDF/PFSA	Direct blended	The anti-fouling property of PVDF-PFSA-H membrane was superior to PVDF-PFSA-Na	[26]
PVDF/PMMA	Direct blended	The good blending of both polymers is due to the presence of basic oxygen in PMMA and an acidic hydrogens in PVDF, thus enabling H-bond interactions. These membrane resulted lower fouling and enhanced permeate quality with lower COD as compared to a PVDF membrane.	[27]
PEI/SPEEK	Direct blended	The hydraulic permeability ($L_{h)}$increased from $24x10^{-11}$ to $36x10^{-11}m^3s^{-1}N^{-1}$.	[28]
CA/SPES	Direct blend UF membrane	This group achieved membranes presenting a 29-69 kDa MWCO and an increase in hydraulic permeability.	[29]

In summary, the blend of two different polymers confers important characteristics such as structure alteration and antifouling properties to UF membrane. The interest of these studies is to generate membranes ,that in addition to separate emulsion by size exclusion. Moreover, this showed also the low flux decline, low fouling due to electric exclusion by means of having surface and pore charge of the same sign as emulsion charge.

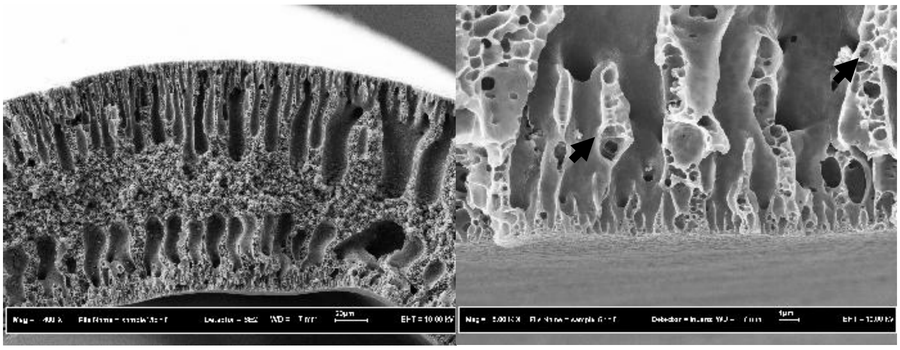
2.1.2 Polymer/Inorganic Composite Membrane

The dispersion of inorganic particles in the polymer matrix have been useful in the improvement of membrane performance. The preparation of membranes formed by inorganic particles uniformly dispersed in a polymer matrix has received much attention from several years. There are many inorganic nano-particles which have been used to prepare polymeric membrane such as TiO_2, SiO_2, Al_2O_3, Fe_2O_3, and ZnO[30,31]. Beneficial effects of certain types of nanoparticles on membrane modification have been reported, such as the amelioration of surface hydrophilicity and enhancement of antifouling property [32-34].

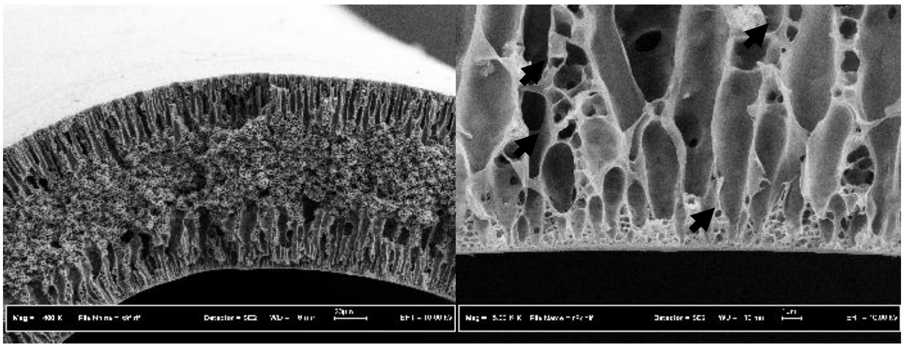
2.1.2.1 Polymer membrane with addition of titanium dioxide (TiO_2)

In recent years, TiO_2 nanoparticles have been commonly used to degrade contaminants in water treatment processes [35]. Several studies have demonstrated that the TiO_2-doped membranes [36-38].Wei et al. [39] prepared the modified PVDF membranes by adding different amounts of TiO_2nanowire into the casting solution, and investigated their bacterial, photocatalytic and anti fouling properties. Results showed that TiO_2 particles addition significantly affected the pore size and hydrophilicity of the membrane and thus improved the flux and permeability of the modified PVDF/TiO_2 membrane. TiO_2-doped PVDF membrane also showed better bactericidal and antifouling abilities under UV light exposure compared with the neat PVDF membrane.

The effect of membrane characterization parameters on permeability and rejection was also investigated using submerged UF experiments by Yuliwati et al. [36]. As shown in Figure 2, PVDF with addition of 1.95 wt.% TiO_2 (PTL-10) and 2.85 wt.% TiO_2 (PTL-15) showed fluxes of 146 L/m^2 h and 82.97L/m^2 h, respectively. The rejection values demonstrated the similar trend to the flux, showing the maximum value of 98.8 % at 1.95 wt.% TiO_2 concentration (PTL-10). It is interesting to note that the observed trend is contrary to the trade-off effect, by which rejection should decrease as flux increases. It is easy to understand that the flux shows a maximum value for the membrane PTL-10, since both porosity and pore size become the highest for this particular membrane [36]. The maximum in rejection occurring at the same TiO_2 concentration, on the other hand, can be explained by the trend observed in the surface hydrophilicity. Most likely, water is preferentially transported through the membrane as compared to the hydrophobic components of the refinery waste water when the membrane surface is hydrophilic, thus the highest rejection of oily components corresponds to the highest surface hydrophilicity of the membrane.



(a)



(b)

FIGURE 2 The cross-sectional and outer surface images of hollow fibers (Mag. 800x) (a) PTL-10 and (b) PTL-15

TiO_2 particles on the membrane surface reduced the interaction between contaminants and the membrane surface. The increased membrane hydrophilicity and membrane pore size with lower TiO_2 concentration (≤1.95 wt.%) could attract water molecules inside the composite membrane; facilitated their penetration through the membrane, enhancing the flux and rejection. However, higher TiO_2 concentration (> 1.95 wt.%) resulted in the formation of a highly viscous dope.

2.1.2.2 Polymer membrane with addition of silver nanoparticles

Silver has been known to be a bactericide since ancient times. Recently, nanosized silver nanoparticles have been reported to exhibit antimicrobial properties [40]. The incorporation of Ag nanoparticles into various matrices has been intensively investigated to extend their utility in materials and biomedical applications [41,42]. Xue et al. [43] reported antimicrobial Ag nanoparticles immobilized on textile. Antibacterial test showed that the as-fabricated textiles had high antibacterial activity against the gram-negative bacteria, *Escheria coli*.

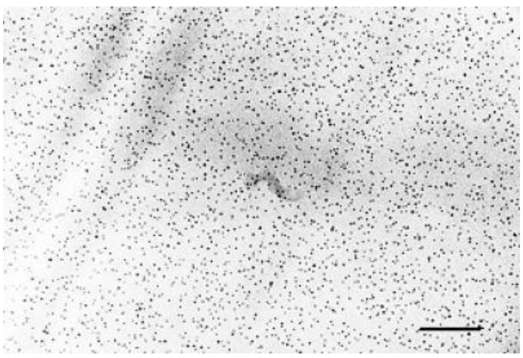


FIGURE 2.5 Polymer membrane with silver nanoparticles

2.1.2.3 Polymer membrane with addition of zinc-oxide nanoparticles

Zink oxide (ZnO), with the completely hydrophilicity, is one of the most common raw materials in industry and suitable to be used to improve the hydrophilicity of the membrane. Furthermore, nanosized ZnO possesses not only the anti bacterial nature but also the valuable ultravioresistant property [44,45], which might potentially benefit the antifouling performance and extend the service life and application field of membranes. Moreover, nano-ZnO is much cheaper than TiO_2 and Al_2O_3 (Alumina) nanaoparticles (1/4 price according to the chinese market quotes). However, the related application of nano-ZnO for membrane modification has not been reported.

Liang et al. studied a novel anti-irreversible fouling PVDF membrane with addition of nano-ZnO as an additive, was succesfully fabricated using non-solvent induced phase separation (NIPS) method [31]. The modification of internal surface of membrane pores was primarily concerned. Different dosage of nano-ZnO ranging from 6.7% to 26.7% (percentage of PVDF weight) was adopted for membrane modification. The filter ability and anti-irreversible fouling property of the resultant membranes were evaluated through testing water permeability, flux recovery and longterm filtration performance by dead-end filtration system. The sample membrane disk was precisely installed in a stirred dead-end cell (Amicon 8400, USA) with an effective membrane area of 41.8 cm^2 and constant strirring speed of 200 rpm at room temperature. All the modified membranes achieved almost 100% water flux recovery after physical cleaning, whereas the raw membrane only reached 78% recovery. The water permeability of the modified membrane almost doubled by adding 6.7% nano-ZnO which was determined as the optimum dosage for PVDF membrane modification. Additionally, the mechanical strength of was found reinforced for modified membrane.

2.1.2.4 Polymer membrane with addition of silica nanoparticles

The addition of fine silica particles (SiO_2) to polyvinylidene fluoride (PVDF) casting solution on some properties of the resulting composite membranes was reported by Bottino et al.[33]. Increasing amounts of SiO_2 (ranging from 10 wt.% to 20 wt.%) added to more diluted 10 wt.% PVDF solutions yield membranes with permeate flux of 80 L/m^2h to 400 L/m^2h. Better retention of 45% was resulted by 3 g SiO_2 added to 100 g PVDF in N-methylpyrrolidone (NMP). These more relevant and beneficial effects due to the silica lies on the increase of the viscosity of the casting solutions that makes easier casting operations thus allowing the preparation of membranes not only with high mechanical properties but also with both better flux and retention.

2.1.2.5Polymer membrane with addition of carbon nano-tubes

Chemical and physical functionalization of multiwalled carbon nanotubes (MWCNT) has been commonly practiced to achieve better dispersion of carbon nanotubes (CNTs) in polymer matrix [11,46].Carbon nanotubes are micro-meter graphene sheets rolled into a cylinder of nanoscale diameter and capped with spherical fullerenes. CNTs have attracted much attention due to their extraordinary characteristics caused by their unique structure [47]. The CNTs have also been considered as ideal model sorbent system to investigated the effect of pore size and surface characteristics on the sorption and transport properties of the porous solids [48,49]. It has been reported experimentally that advanced water treatment could be applied by using ligned CNTs membranes, which produce nanoporous structure of membrane [48,50].

Table 3
Polymer/Inorganic Composite Membrane

Polymer used	Method	Remark	Reference
PVDF/TiO_2	Phase inversion method	TiO_2 loading increased hydrophilicity and fouling resistance of membrane. The maximum flux of 146 L/m^2h was achieved with addition of TiO_2 of 1.95 wt.%.	[36]
PSf/PVP/TiO_2	Phase inversion method with direct blended of TiO_2	The membranes with addition of TiO_2 demonstrated an excellent anti-fouling performance (>90%) and particularly reducing teh fouling resistance	[50]
PES/TiO_2	Photocatalytic TiO_2 powder		[38]
PVDF/ZnO	Phase inversion method	The implantation of nano-ZnO into membrane inner surface demonstrated the enhancement of anti-irreversible fouling property. The water permeability of modified membrane almost doubled by adding 6.7% nano-ZnO to PVDF membrane.	[31]
PVDF/SPES/TiO_2	Phase inversion method	The presence of 4wt.% TiO_2 in membrane structure demonstrated the increase of hydrophilicity, thus possess the dramatic photo-bactericidal effect on *Escherichia coli (E.coli)*	[51]
PS/SiO_{2+}	Phase inversion method	The effective pore radius of	[52]

		the membrane increased when the silica concentration in the casting solution is increased.	
PVDF/CNTs	Phase inversion method	The highly dispersion of CNTs in polyvinylidene fluoride occurred based on the immobilization the nanotubes in the pore structure. The importance of the size and uniformity of the nanotubes plays a big role in manufacturing processes for carbon nanotubes in polimeric matrices.	[11]

3.0 Summary

Membrane materials are currently the most important part in membrane technology and it was experiencing significant growth. Generally the development of membrane materials can be divided into two periods according to research activity: (i) the search for a suitable material (chemical composition) and membrane formation mechanism (1960s to late 1980s), and (ii) the evolution of more controlled conditions for membrane formulation to enhance membrane functionality and durability (late 1980s to date).[1] The selection of membrane material allows control over the nature and magnitude of the permeant-membrane physicochemical interaction. However, it would be beneficial if one could experimentally verify that the proper choice has been made prior to undertaking the often difficult tasks of membrane preparation and characterization. The objective of this chapter is to review the current development of membrane materials for ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) that is helpfull to choose the suitable type of material.

Choise of membrane material, i.e. polymer, copolymer, inorganic, polymer/polimer, and polymer/inorganic, also determines the packing density and segment mobility of the materials chains, which comprise the solid regions of the membrane. This influences the mechanism of transport, membrane stability and membrane performance that often follows a common sense approach. The number of polymers has been studied in recent literatures and patents, which indicated that an ever-increasing number of polymers, copolymers and blends are being considered as potential membrane materials for liquid mixture separations. The application of polymeric material for a separation membrane depends of course upon both the throughput and the purity of the product transported through membrane. The most widely used polymers for commercial ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membrane are polysulfone (PSf), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyetherimide (PEI), polyacrylinitrile (PAN), Cellulose Acetate (CA), polyamide (PA), polyfurane, polyether-polyfurane, polyvinylamine, polypyrrolidine, polypiperazine amide. Inorganic (nanoparticle) materials are used to membrane preparation as follows, titanium dioxide (TiO_2), zinc oxide (ZnO) nano-particles, silica oxide (SiO_2), alumina (Al_2O_3), and carbon nano-tubes (CNTs).

The emergence of nano-technology in membrane materials science could offer an attractive alternative to polymeric materials. Recent opinion in nano-technology is, that it deals with structures having at least one dimension that is sufficiently small, the order about one to several hundred nanometers. It is concerned with materials and systems, which have structures and components exhibit novel and significantly improved physical, chemical, and biological properties in order to exploit of novel phenomena and processes due to their nanoscale sized. There are a large number of nanofiltration membrane application made from a polymeric or an inorganic material for UF, NF and RO membranes. It is proposed that these novel materials represent the most likely opportunities for enhanced membrane filtration performance in a current trend and the future.

Nomenclature

PSf	—	Polysulfone
PES	—	Polyethersulfone
PAN	—	Polyacrylonitrile
PS	—	Polystyrene
PC	—	Polycarbonate
PVDF	—	Polyvinylidene fluoride
PMMA	—	Polymethylmetacrylate
SPEEK	—	Sulfonated polyether-ether-ketone
PFSA	—	Perfluorosulfonic acid
PEI	—	Polyetherimide
SPEI	—	Sulfonated polyetherimide
SPC	—	Sulfonated polycarbonate
TiO_2	—	Titanium oxide
ZnO	—	Zinc oxide
SiO_2	—	Silica oxide
Al_2O_3	—	Alumina
UF	—	Ultrafiltration
NF	—	Nanofiltration
RO	—	Reverse osmosis
CNTs	—	Carbon nano-tubes

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