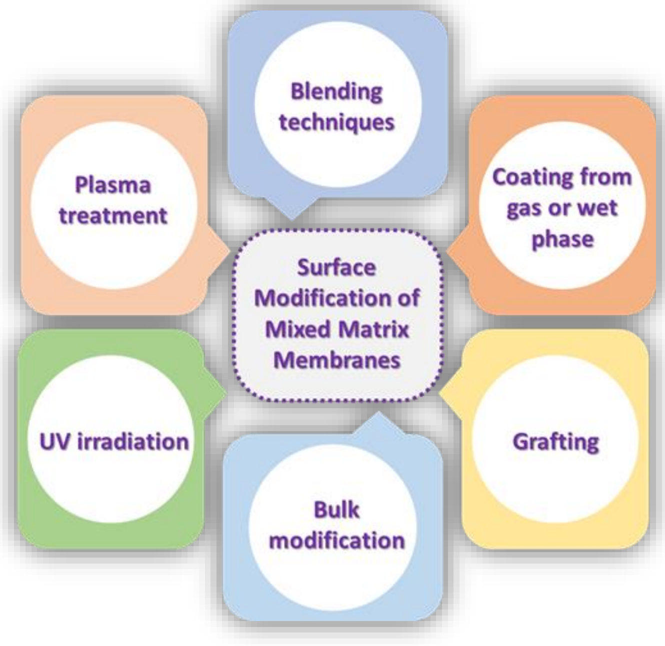
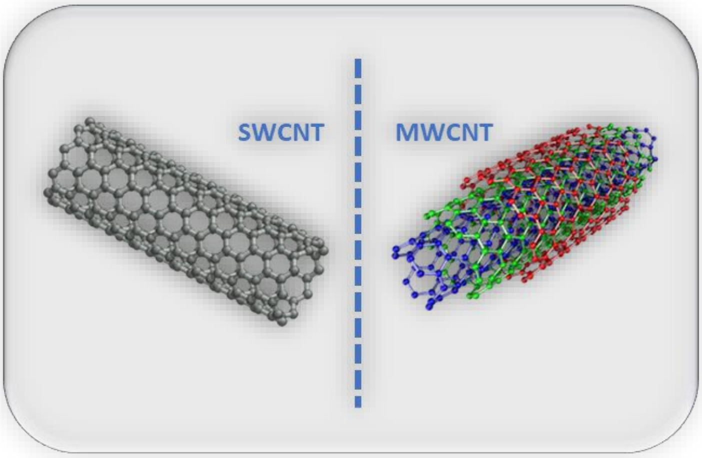


Chapter 1

Introduction



1.1. Polymeric membranes

Polymeric membranes are thin, selective barriers made from various types of polymers that are used to separate, purify, or concentrate different substances in a mixture. These membranes are widely employed in various industries including water treatment, gas separation, food and beverage processing, and pharmaceuticals. They allow specific molecules or ions to pass through while blocking others, depending on their size, charge, or other properties.

Polymeric membranes are type of synthetic membrane which are widely used in the membrane-separation industry. Membrane materials can be typically classified into three main categories: organic (polymeric), inorganic (ceramic), and biological. Polymeric membranes are preferred due to their high selectivity, ease of operation, customization, and modification capabilities, among other benefits[1,2].

1.1.1 Classification of polymeric membranes

Polymeric membranes can be categorized depending on their surface chemistry, internal structure, shape, and method of manufacture. The selection of the membrane polymer is critical and depends on the intended application. The polymer should have certain qualities, including a low tendency to bind with separated molecules, the ability to endure harsh cleaning circumstances, and conformability with the chosen membrane manufacturing technology. The polymer must also be a suitable membrane former in terms of its chain rigidity, chain interactions, stereoregularity, and polarity of its functional groups. Polymers can exist in a range of structures, from amorphous to semi-crystalline, and may have varying glass transition temperatures, which can impact the performance characteristics of the membrane. Membranes can be synthesized as either amorphous or heterogeneous structures, regardless of whether they are dense or not.

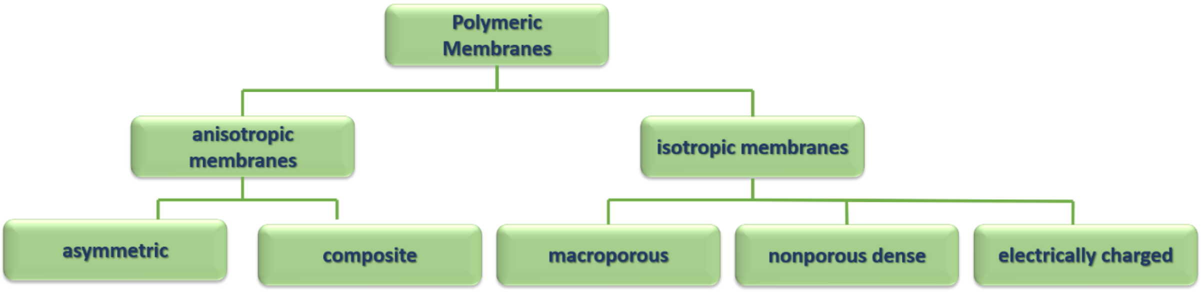


Figure 1.1. Classification of polymeric membranes[3]

Figure 1.1 shows five types of polymeric membranes, including three isotropic and two anisotropic. Isotropic membranes are uniform throughout their volume and can be categorized into three categories: macroporous, nonporous dense, and electrically charged. A macroporous isotropic membrane features a network of interconnected cylindrical pores within the material, allowing for the selective transport of molecules or ions. Nonporous dense isotropic membranes lack pores and are impermeable to the passage of molecules and ions. An electrically charged isotropic membrane which has an electrical charge, influencing the transport of charged species, while anisotropic membranes exhibit a non-uniform structure, either chemically and/or structurally heterogeneous. The two types of anisotropic membranes showed in the diagram are asymmetric and composite. Asymmetric membranes made up of a thin dense film of a highly cross-linked polymer on the surface of a thicker microporous substrate. The dense polymer layer function as a barrier to the passage of molecules or ions, while the porous layer enables selective transport. A composite membrane is composed of two or more layers of different materials, each with unique properties. The layers can be arranged in various ways to achieve different properties, such as high selectivity or high flux.

1.1.2 History of polymeric membranes

Polymeric membranes have a long history of development and application in various fields, with multiple polymers investigated for membrane fabrication, including conventional polymers such as cellulose acetate, polysulfone, polyethersulfone, polyvinylidene fluoride, cellulose diacetate, cellulose triacetate, polyamide, polyetheramines, and polypropylene, as well as more recently, sustainable polymers. Polymer-based membranes play a significant role in water purification, fuel cells, and batteries, where they control the selective transport of ions and/or water. The first viable reverse osmosis (RO) membrane was fabricated using cellulose acetate (CA) and developed into an integrally skinned asymmetric semi-permeable membrane by Loeb and Sourirajan at UCLA in 1959, and patented in 1960[4]. John Cadotte of North Star Technologies (later FilmTec Corporation) developed the first interfacial polyamide (IP) thin-film-composite (TFC) membrane in 1972. TFC membranes are composed of multiple layers, with those designed for desalination utilizing an active thin-film layer of polyamide layered with polysulphone as a porous support layer. Thin film composite (TFC) membranes have undergone tremendous development since the concept of interfacial polymerization (IP) was first introduced, and are used in various applications, including desalination, gas separation, and nanofiltration.

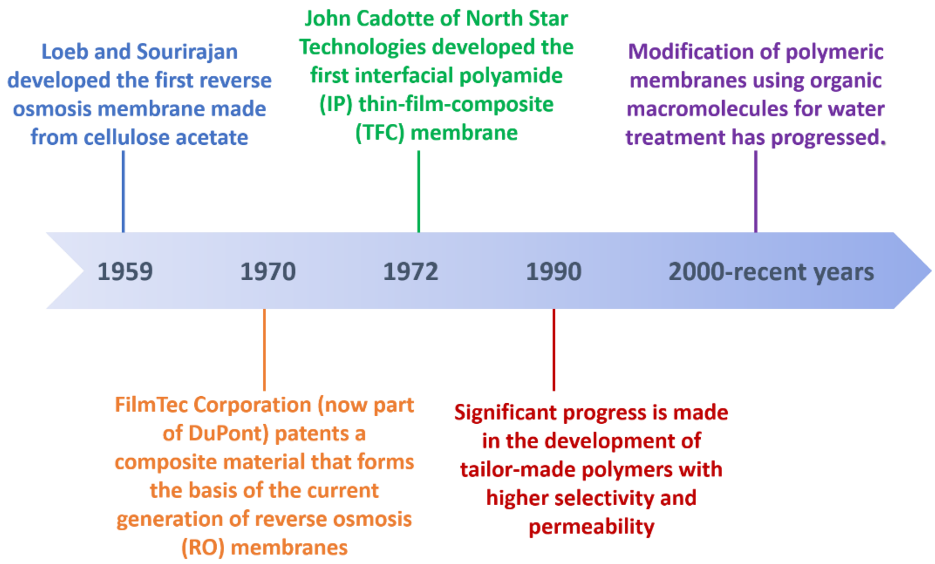


Figure 1.2. Milestones in the development of polymeric membranes

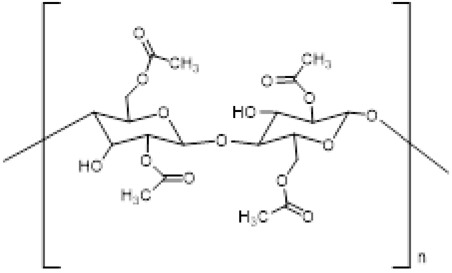
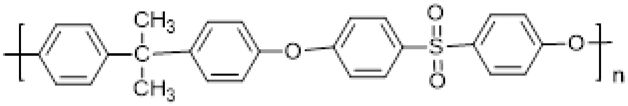
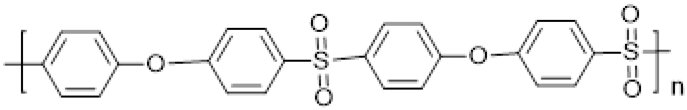
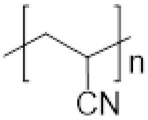
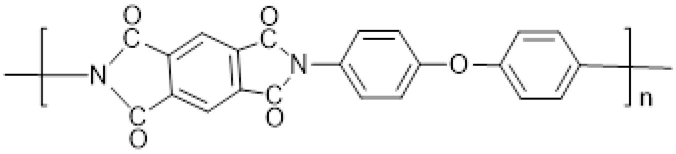
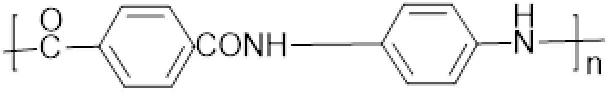
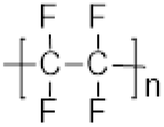
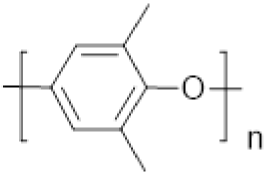
1.1.3 Mixed Matrix Membranes (MMMs)

Mixed matrix membranes (MMMs) are a type of membrane material that consist of inorganic fillers dispersed in a polymer matrix. These heterogeneous membranes combine the processability of polymers with the separation properties of molecular sieves, and they are utilized for gas separation. MMMs have been found to have higher selectivity and permeability than traditional polymeric membranes[5,6]. To optimize the performance of MMMs, it is necessary to change the physical and chemical properties of the polymeric material as well as the nanomaterial size and shape of the polymer matrix to achieve a better interface. The intention behind incorporating secondary chemicals/components into the polymer matrix through dispersion is to enhance the properties of the polymeric membrane. Mixed matrix membranes (MMMs) offer several advantages over traditional membranes, including improved selectivity and permeability, enhanced performance, scalability, and cost-effectiveness[7]. The fabrication of MMMs involves adding inorganic fillers such as zeolites, metal-organic frameworks (MOFs), silica-based materials, carbon-based materials, and metal oxides to a polymer matrix. The idea of mixed matrix membranes (MMMs) was first proposed in the 1990s by Zimmerman et al. as a solution to overcome the limitations of traditional membrane materials such as polymeric and thin film composite membranes[8].

1.2 Polysulphones

Various polymers are used for the membrane preparation such as Polysulphone (PSU), Polyether sulphone (PES), Polyacrylonitrile (PAN), Polyphenylene oxide (PPO), Polyimides (PI) and Polyamides (PA), Polytetrafluoroethylene (PTFE), etc.

Table 1.1. Polymers used for membrane preparation

Polymer	Repeating Unit	Tg (℃)
Cellulose Acetate (CA)		199
Polysulphone (PSU)		190
Polyether sulphone (PES)		230
Polyacrylonitrile (PAN)		97
Polyimide (PI)		222
Polyamide (PA)		49
Polytetrafluoroethylene (PTFE)		117
Polyphenylene Oxide (PPO)		209

1.2.1 Polysulphone (PSU)

Polysulphone (PSU) is a widely used polymer in phase-inversion membranes due to its commercial availability, ease of handling, favorable selectivity-permeability characteristics, and high glass transition temperature of 190°C. It has strong mechanical, thermal, and chemical properties, making it a high-performance thermoplastic known for its toughness and stability at high temperatures[9,10]. Polysulphone belongs to a family of polymers that contain an aryl-SO_2-aryl subunit and has outstanding resistance to heat and oxidation, hydrolysis resistance in aqueous and alkaline media, and good electrical properties. It is highly resistant to degradation by hot water and steam and also resistant to aqueous mineral acids, bases, and oxidizing agents.

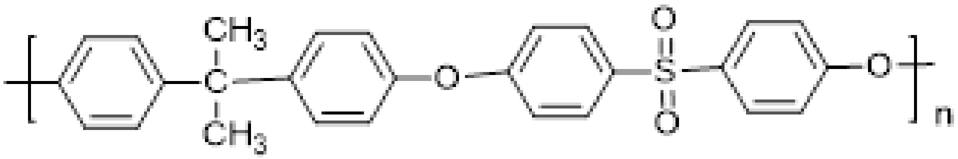


Figure 1.3. Structure of Polysulphone (PSU)

Polysulphones are typically prepared by polycondensation of diphenoxide and bis(4-chlorophenyl) sulphone (DCDPS). The sulphone group in DCDPS activates chloride, allowing it to react with diphenoxide to form polysulphone. Polysulphone membranes are widely utilized in various applications, like water treatment, hemodialysis, food and beverage processing, gas separation, and in the automotive and electronics industries. Their properties like stability, mechanical strength, and chemical stability make them suitable for specialized applications. Polysulphone membranes are commonly used in processes like microfiltration[11,12], ultrafiltration[13–15], nanofiltration[16,17] and reverse osmosis (RO) to remove impurities from water. However, polysulphone membranes are prone to fouling, which refers to the accumulation of particles or microorganisms on the surface of the membrane, leading to reduced performance. The surface characteristics of the membranes, such as hydrophilicity and charge, can affect the fouling behaviour. Modifying these surface characteristics can improve the antifouling behaviour of polysulfone membranes for specific applications. Also the permeability of polysulphone membranes can be optimized for specific applications by modifying their surface properties, which are affected by factors such as pore size, surface hydrophilicity, and surface charge[18].

1.2.2 Polyether sulphone (PES)

Polyether sulphone (PES) also exhibits very good chemical and thermal stability as demonstrated by its glass transition temperature (Tg) of 230℃. This polymer is also commonly used as supporting material for composite membranes. Polyether sulphone (PES) is a high-performance polymer that belongs to the polysulfone family. It is an amorphous, transparent, and rigid thermoplastic that is tough, dimensionally stable, and has bonds with high thermal and oxidative stability. The sulphone group provides high-temperature performance, while the ether linkage allows for mobility of the polymer chain in the melt phase. PES is highly resistant to heat, oxidation, and hydrolysis in aqueous and alkaline media and has good electrical properties. PES can be synthesized through a nucleophilic aromatic substitution reaction between dihalogenated diphenylsulfones and bisphenol-type compounds or by self-polycondensation of AB-type monomers[19].

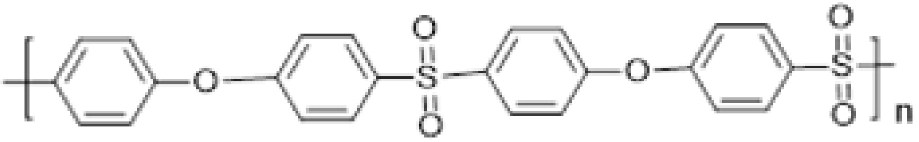


Figure 1.4. Structure of Polyether sulphone (PES)

PES membranes possess several benefits over other membranes in microfiltration applications, such as superior properties, hydrophilic properties, versatility, high flow rate, and consistent filtration performance. These benefits make PES membranes a suitable choice for various applications such as microfiltration[20,21], ultrafiltration[22–24] and nanofiltration[25–27]. To improve the performance of PES membranes in wastewater treatment applications, they are often surface-modified with various protected chemistries to reduce protein adsorption and membrane fouling by increasing their resistance[28].

Both Polysulphone and Polyether sulphone are commonly used in the asymmetric membrane preparation process through phase inversion using water as a coagulant bath. Although both are amorphous thermoplastics with similar properties, PSU is more heat-resistant and has better stiffness and stability compared to PES. The choice between PES and PSU depends on the particular requirements of the application.

1.3 Membrane preparation methods

Various preparation techniques exist, such as sintering, stretching, track etching, template leaching, and dip coating, which used for the fabrication of a membrane from a specific material and with the desired morphology[29–35]. Phase inversion techniques are among the most widely used and versatile methods for membrane preparation, applicable to a broad range of polymeric materials. The asymmetric membrane may have a thin, dense skin layer formed via dry or wet phase inversion processes, such as solvent evaporation, vapor precipitation, controlled evaporation precipitation, thermal precipitation, and immersion precipitation. Immersion precipitation is one of the first commercialized techniques and is commonly used to prepare several membrane morphologies, making it one of the most common methods of membrane formation[36,37].

Phase inversion involves transforming a homogeneous polymer solution into a porous structure by changing the solvent-nonsolvent ratio or temperature. Several variations of phase inversion are outlined below.

1.3.1 Precipitation by solvent evaporation

Precipitation by solvent evaporation is a commonly used method for creating membranes. This process involves dissolving a polymer in a solvent and nonsolvent mixture, then evaporating the solvent to produce the polymer. This method has several advantages, such as the capacity to produce consistent and unadulterated items, ease of use, and affordability. Nonetheless, it also has some drawbacks, including the need to remove the product, the production of salty solutions, and challenges in regulating the evaporation rate. The use of these membranes is diverse and includes applications such as microfiltration, pervaporation, and gas separation[38].

1.3.2 Precipitation from Vapour phase

The process of precipitation from the vapor phase involves the formation of membranes by condensation of vapor-phase materials. There are two known types of vapor-phase precipitation: physical vapor deposition (PVD) and chemical vapor deposition (CVD). PVD involves the deposition of material in the vapor phase onto a substrate, whereas CVD involves the chemical reaction of vapor-phase precursors to form a membrane. In the case of phase-inversion membranes, a solvent-polymer mixture is cast on a film and placed in a vapor atmosphere containing a nonsolvent saturated with the same solvent. The high concentration of the solvent in the vapor atmosphere prevents the solvent from evaporating, and the membrane forms through the diffusion of the nonsolvent into the cast film. Precipitation from the vapor phase can yield symmetric microporous membranes, whereas immersion precipitation typically results in asymmetric ultra- or skinned membranes.

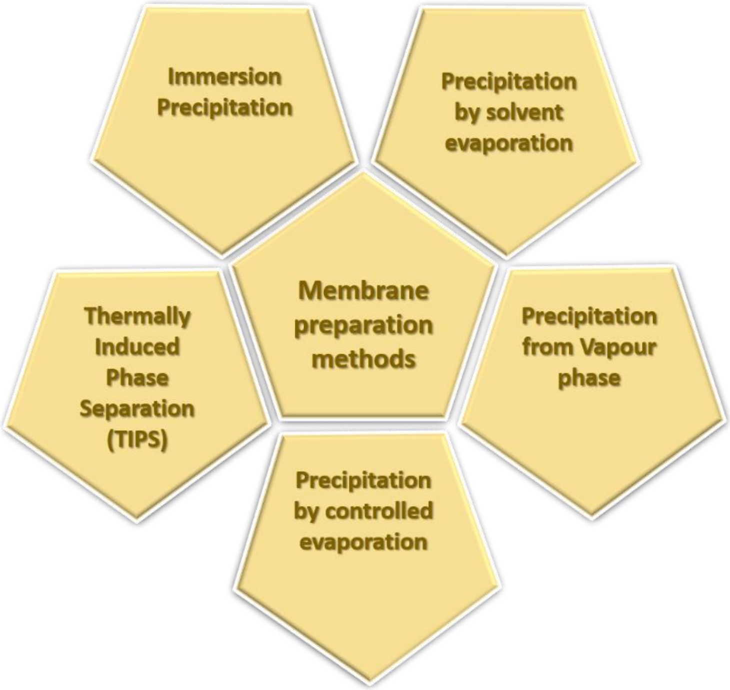


Figure 1.5. Various membrane preparation methods

1.3.3 Precipitation by controlled evaporation

The process of precipitation by controlled evaporation is utilized to prepare membranes. This technique involves dissolving a polymer in a solvent and nonsolvent mixture, followed by the evaporation of the solvent under controlled conditions to precipitate the polymer. The resulting membrane can be used in microfiltration. The combination of phase separation and mass transfer affects the membrane structure. Although effective and simple, this technique has limitations, including a long sample preparation time, limited control over membrane structure, difficulty in scaling up, and limited solvent options[39,40].

1.3.4 Thermally Induced Phase Separation (TIPS)

Thermally Induced Phase Separation is a widely used technique for preparing membranes. The process involves using a diluent or "latent solvent," heating the solution to a temperature above the melting point of the polymer, and cooling the solution to a temperature below the melting point of the polymer to cause phase separation and form a porous membrane. This technique can form highly porous microporous membranes, and the membrane morphology can be tailored for specific applications. This technique is a cost-effective and scalable method for preparing membranes, and it is often used to make microfiltration membranes[41,42].

1.3.5 Immersion Precipitation

Immersion precipitation, a widely used method for preparation of membranes, involves casting a polymer with a solvent on a proper supporting layer and then submerging it in a coagulation bath containing a nonsolvent. This process results in precipitation, and the polymer eventually forms a porous thin film membrane. The membrane morphology is affected by the combination of phase separation and mass transfer. Immersion precipitation is the most commonly used membrane preparation method and can be used to prepare a wide range of membranes, including cellulose acetate, polysulfone, polyethersulfone, and polyvinylidene fluoride. This method has various advantages, such as versatility, a variety of polymers, a simple process, and asymmetric membrane formation. Asymmetric membranes exhibit a thin, dense layer on one side and a porous layer on the other, which can improve their separation performance[43–46].

1.4 Carbon nanotubes (CNT)

In 1991, a scientist named Iijima from NEC Laboratory in Japan used High-Resolution Transmission Electron Microscopy (HRTEM) to discover tiny structures called carbon nanotubes[47]. Almost at the same time in 1992, researchers from Russia also found similar structures, which nanotubes but smaller length to diameter ratio[48,49]. A big development happened in 1996 when a group led by Smalley at Rice University managed to create groups of straight carbon nanotubes that were very thin and well-arranged[50].

Carbon nanotubes are allotropes of carbon with tubular nanostructures. These nanotubes are extremely strong, conduct heat and electricity well, and are useful fillers. They are part of a family of structures called fullerenes. The walls of CNTs are incredibly thin sheets of carbon, such as graphene, which is also an allotrope of carbon with unique bonds. These sheets are curled at specific angles to form different types of nanotubes, like zigzag and armchair. The bonding in carbon nanotubes is primarily composed of sp^2 hybridized covalent bonds between the carbon atoms. This bonding arrangement is responsible for the unique structural, mechanical, and electronic properties of the CNTs. Carbon nanotubes may display inter-tube bonding, which results in the creation of bundles of CNTs, a phenomenon worth mentioning.

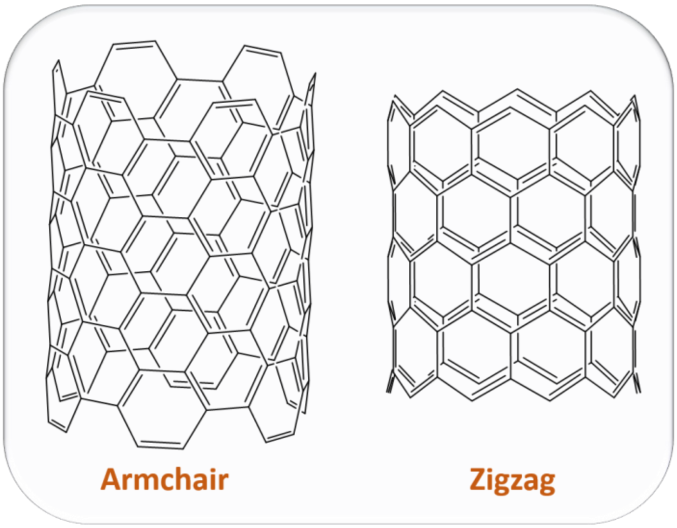


Figure 1.6. Carbon Nanotubes (CNTs)

Both zigzag and armchair carbon nanotubes possess distinct structures and electrical properties. Zigzag carbon nanotubes have alternating zigzag patterns along their edges and exhibit magnetic field-induced conductivity oscillations, while armchair carbon nanotubes feature an armchair pattern along their edges and are considered to be metallic.

Carbon nanotubes (CNTs) are generally classified into two types: single-walled carbon nanotubes and multiwalled carbon nanotubes. The nanotubes are held together by a relatively weak bond known as Van der Waals forces, specifically π-stacking.

1.4.1 Single Walled Carbon Nanotubes (SWCNTs)

The structure of single-walled carbon nanotubes (SWCNTs) can be visualized as a cylinder made by rolling a graphene sheet, which is only one atom thick, into a seamless tube. This process is represented by a pair of indices (n, m), which indicate how the graphene is wrapped around the cylinder. The letters n and m represent whole numbers that show how many unit vectors move in two directions across the honeycomb pattern of graphene. The diameter of the SWCNTs can be calculated from the following equation,

$$d = \frac{a}{\pi}\sqrt{(n^2 + nm + m^2)} = 78.3\sqrt{((n+m)^2 - nm)}\,pm$$

Where, a= 0.246 nm. When n and m are the same, the nanotubes are called armchair. If m is zero, it is called a zigzag. Otherwise, they are considered chiral.

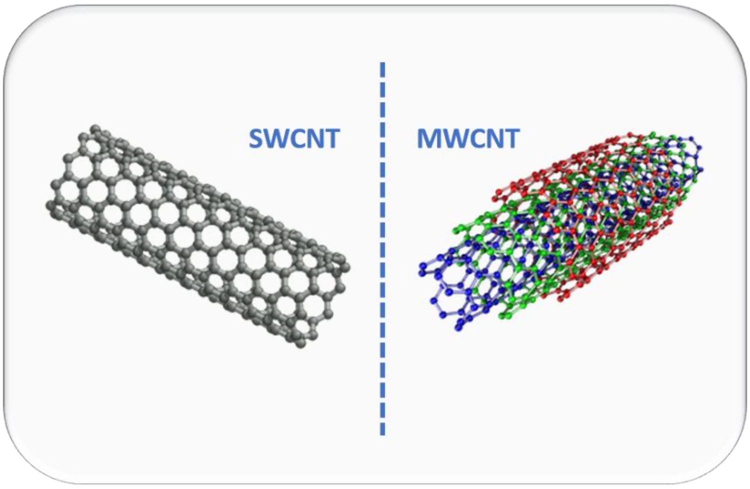


Figure 1.7. Single walled carbon nanotubes (SWCNT) and Multiwalled carbon nanotubes (MWCNT)

1.4.2 Multi-walled Carbon nanotubes (MWCNTs)

Multi-walled carbon nanotubes (MWCNTs) are a type of carbon nanotube that consists of multiple layers of graphene rolled into a tube-shaped structure. The number of layers can range from a few to tens, and its diameter ranges from 1-3 nanometers for the inner diameter and 2-100 nanometers for the outer diameter, with a length of 5-10 micrometers. MWCNTs exhibit properties that differ from single-walled carbon nanotubes (SWCNTs), as they generally exhibit a combination of metallic and semiconducting behaviour because of the presence of multiple layers. The properties of MWCNTs are influenced by factors like the number of layers, diameter, and defects within the structure. MWCNTs have numerous applications in fields including electronics, energy storage, composite materials, and biomedicine. Their properties and unique structures make them suitable for enhancing the mechanical, electrical, and thermal properties of materials, as well as for application in sensors, catalyst supports, and drug delivery systems.

MWCNTs can be produced through various methods such as chemical vapor deposition (CVD), arc discharge, or laser ablation. The production process can affect the diameter, length, and quality of the MWCNTs.

1.4.3 Methods for Carbon nanotubes synthesis

The initial methods for producing carbon nanotubes involved high-temperature techniques like arc discharge and laser ablation. However, these approaches had some limitations as they could not precisely control the orientation, length, diameter, arrangement, purity, and quantity of nanotubes produced. Consequently, the low-temperature chemical vapor deposition (CVD) method has become more popular than other older methods. In all of these techniques, the process of making carbon nanotubes includes adding impurities (such as other carbonaceous particles like nano crystalline graphite, amorphous carbon, fullerenes, metals like Fe, Co, Mo, Ni) used as catalysts during the formation of carbon nanotubes[51]. Unfortunately, these impurities can affect the desired properties of the carbon nanotubes and also make it challenging to analyze and use them. Therefore, a significant challenge in carbon nanotube research is finding ways to purify them effectively and simply[52]. The most successful and commonly used purification technique involves treating the nanotubes with acids.

A. Arc discharge method for the MWCNTs synthesis

The arc discharge method of MWCNT utilizes a DC arc discharge between two water-cooled graphite electrodes with diameters of 6 and 12 mm in a chamber filled with helium at sub-atmospheric pressure. The properties and morphology of MWCNT vary based on the conditions and atmosphere used. Wang et al. performed DC arc discharge of graphite electrodes in He and methane, resulting in thick nanotubes with many carbon nanoparticles under high-pressure methane gas and a high arc current. However, thin and long MWCNTs were produced under a methane gas pressure of 50 Torr and an arc current of 20 A for the anode with a diameter of 6 mm[53]. Zhao et al. compared the formation of fine and long MWCNT under a H_2 gas atmosphere with He and CH_4 atmospheres, reporting that little carbon smoke was obtained in the case of H_2 gas, while more carbon smoke was obtained in the case of evaporation under, He and CH_4 gases[54]. Pulsed techniques have also been reported, including the single-pulse arc production of near vertically oriented MWCNT deposited on Ni/glass samples using a graphite counter-electrode in ambient air by Parkanshy et al. MWCNTs with a diameter of about 10 nm and lengths of up to 3 μm were produced on the samples with a single 0.2 μs pulse[55]. Tsai et al. also reported single pulse discharge in air, resulting in MWCNTs with an outer diameter of 17 nm and an inner diameter of 5 nm using a peak current of 2.5A and a discharging time of 1000 μs[56]. The arc discharge method is a popular and simple approach for creating carbon nanotubes, but it generates a mixture of components that require further purification to separate the nanotubes from soot and residual catalytic metals.

B. Laser ablation

Laser ablation is another method used to synthesize carbon nanotubes. The method was first demonstrated by Smalley et al. in 1995 and operates on similar principles to the arc-discharge method[57]. Instead of an electric arc, a laser provides energy to a graphite pellet containing Ni or Co catalyst materials[58]. The high-power laser vaporizes the graphite target, converting it into carbon-metal vapor with extremely high temperatures. The vapor is then rapidly cooled, resulting in the formation of carbon nanotubes through vapor condensation. Laser ablation can yield up to 70% by weight of single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature. However, it is a more expensive method compared to arc discharge or chemical vapor deposition[59,60].

C. Chemical Vapor deposition (CVD)

The discovery of chemical vapour deposition (CVD) process took place in the 1950s, although the discovery of carbon nanotubes (CNTs) by this method occurred in 1993[61]. In this method, a reactor bed consisting of a layer of metal catalysts, such as Ni, Co, Fe, or a mixture of these metals, is used. The diameter of the nanotubes depends on the size of the solid particles used. High-temperature annealing of the substrate is performed at 700 °C, and a combination of inorganic or process gases (i.e., N_2 and H_2) and organic gas (i.e., methane, ethene, or ethyne) is used as an initiator for the growth of nanotubes at metal particles. The catalyst particles can stay at the tips of the growing nanotube during the growth process or remain at the nanotube base depending on the adhesion between the catalyst particle and the substrate[62]. The catalyst is responsible for initiating the decomposition of the carbon source in the CVD process, which can be achieved through either thermal CVD or plasma-enhanced CVD (PECVD) using plasma irradiation. The resulting decomposition leads to the formation of CNTs through the process of nucleation. The growth of CNTs is also affected by the catalyst used in the process. Therefore, its preparation is a decisive step in CNTs synthesis. In this method, carbon-containing gas is decomposed on a substrate or catalyst surface to form carbon nanotubes (CNTs). The thermal CVD method has been demonstrated to synthesize carbon nanotubes (CNTs) on stainless-steel substrates without the addition of an external catalyst[63]. In PECVD, a plasma source is used to create a glow discharge, which activates the precursor gases and promotes the formation of carbon nanotubes. PECVD is extensively used to grow many types of carbon nanotube structures. Carbon nanotube (CNT) growth by chemical vapor deposition (CVD) is the most versatile and cost-effective method currently available. This is because of the simplicity of the equipment, operation, and low cost, as well as its proven ability to produce high-purity single-walled and multi-walled CNTs with well-controlled properties. CVD has broad prospects for large-scale CNT control in recent years[64].

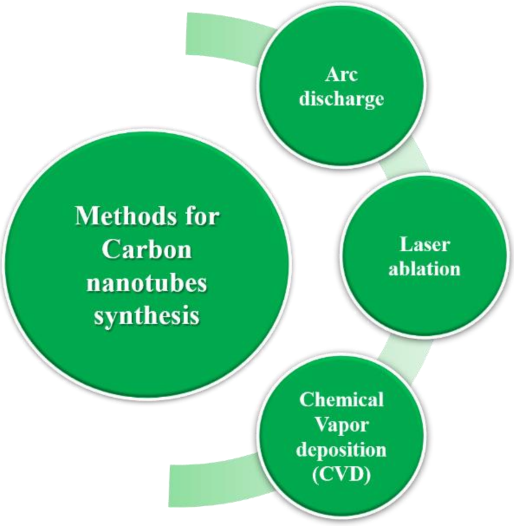


Figure 1.8. Methods for the synthesis of Multiwalled carbon nanotubes (MWCNT)

1.5 Mixed Matrix Membrane incorporated with CNTs literature outline

Owing to their versatile applications in various separation fields, the production of mixed-matrix membranes (MMM) has attracted significant research interest. MMM possess a range of desirable properties, such as the desired tensile strength, better selectivity, good permeability for the preferred gas or liquid, and improved antifouling properties, making them a superior choice for research. Mixed-matrix membranes, which are synthesized by incorporating fillers into the polymer matrix, can be classified as such. The purpose of incorporating secondary chemicals/components through dispersion into the polymer matrix is to enhance the properties of polymeric membranes. Various modifications, such as polymer substitution or post-polymerization, blending with other polymers, and incorporating solid particles, are used to improve the properties and enhance the membrane permeability. However, the most favorable approach is the addition of solid particles to the polymer matrix, which provides a simpler preparative process. MMMs can be utilized in various applications such as waste-water treatment, desalination, gas separation, pervaporation, among others, depending on the type of fillers present. These fillers can be either inorganic materials or other components, and various other types of nanocomposites can be introduced into the membrane matrix to enhance its properties. Different nanoparticles such as silica nanoparticles[65–68], metal-organic frameworks[69,70], carbon nanotubes[71–73], graphene oxide[74,75], silicates[76], zeolites[77], and inorganic materials[78–80] have been introduced. They bind to the polymer matrix by cross-linking covalently or by blocking the pores of the membrane. The nanoparticles are dispersed in the polymer matrix, which increases the porosity.

Nowadays, carbon nanotubes (CNTs) are the most promising material for creating nanocomposite membranes because of their strong π-π stacking interaction with aromatic compounds. Carbon nanotubes (CNTs) has characteristics such as high aspect ratio, low density, and high mechanical strength and stiffness. Many studies have focused on using functionalized carbon nanotubes as fillers because the membranes created exhibit antifouling properties and high rejection of inorganic, organic, and microbiological contaminants. The incorporation of CNTs into the matrix enhances the surface hydrophilicity, permeability, solute rejection, reduces fouling tendency, enhances tensile strength and electrical conductivity, and controls pore size, surface chemistry, and polymer crystallinity. However, the application of CNTs is limited because of their high cost[81].

The functionalized carbon nanotubes, specifically oxidized, amide, and azide/polysulfone MMM, demonstrate improved water flux, rejection, and conductivity. Among the three functionalized nanotubes, the azide-functionalized/polysulfone membrane showed a higher flux and 90% rejection of Pb(II) and 93% rejection of Cu(II) at a lower pH and 4.06 bar pressure. The heavy metal removal capacity of membranes with oxidized, amide, and azide-functionalized MWCNT-incorporated polysulfone (PS) mixed matrix membrane was analyzed at varying pH and transmembrane pressures. The carbon nanotubes concentration was varied from 0.1-1 wt% in the polymeric matrix, and the best rejection was obtained from 1 wt% Azide functionalized/polysulfone membrane at 0.49 MPa and acidic pH 2.6. The Amide functionalized CNT/PS membrane rejected 94.8 % Cr (VI), which was only 10.2% in case of pristine polysulfone membrane. After the addition of functionalized carbon, the flux increases, as well as the hydrophilicity, which is proven by the contact angle measurement, due to the reduced pore size, which shows that these functionalized nanotubes form a physical bond between the polysulfone and functionalized nanotubes[82,83]. Recent studies have shown that small-angle neutron scattering (SANS) can also be used to study the morphology of polyethersulfone/functionalized multi-walled carbon nanotube (MWCNTs) membranes. The pore dimensions, dimensions, porosity, and correlation length of the membrane pores can be analyzed using this tool. Pore dimensions can also be analyzed using capillary flow Porometry, which reveals that pores are more uniform in the MWCNT/Polysulfone membrane than in the pristine membrane. However, this technique was unable to detect small pores. The SANS data was able to overcome this limitation, showing that with an increase in the weight percentage of nanotubes in the membranes, the pore dimensions decrease and the porosity increases, which is in agreement with the percentage of heavy metal removal. The correlation length was determined 3.9 nm, which is the same for the pristine membrane and other functionalized CNT impregnated membranes. This is explained by another study, which suggests that the porosity of the membrane increases with a decrease in pore sizes while keeping the distance between the pores equal. The SANS data also shows that aligned functionalized MWCNTs are uniformly distributed in the PES matrix, which is supported by the high pure water flux, indicating that water molecules pass through the nanotubes and reject heavy metals. The water transportation speed and rejection of heavy metals were also found to be three times higher than in the pristine PES membrane[84,85]. Functionalized single walled carbon nanotubes (SWCNTs) were added to a polysulfone membrane, resulting in high rejection of heavy metals and increased hydrophilicity and thermal stability. During the preparation of the modified membrane, migration of the modified nanotubes at the membrane/liquid interface reduced interfacial energy, causing an increase in the viscosity of the solution and a slower solvent/non-solvent process[86].

A mixed matrix membrane (MMM) that incorporates carbon nanotubes (CNTs) has been used for gas separation studies. The MMMs made with a polysulfone (PSF) matrix and functionalized CNTs (PSF/PEG-g-CNT) showed improved CO_2 permeability and selectivity compared to pure polymer MMMs. They also demonstrated mechanical robustness, making them suitable for further studies in simulated industrial conditions[87]. The MMMs are created by incorporating oxygenated multiwalled CNTs (MWCNTs) into a PSF polymer matrix. The MWCNTs are functionalized with oxygen groups to improve dispersion in the polymeric dope solution. This study investigates the effect of varying the f-MWCNTs concentration on the gas separation performance of MMMs. The results showed that MMMs with 3% w/w MWCNTs had the highest CO_2/N_2 selectivity and permeability. The study concludes that incorporating oxygenated MWCNTs into PSF MMMs can improve their gas separation performance, making them a promising material for CO_2 separation[88,89].

A study presented the groundbreaking integration of forward osmosis in seawater desalination and wastewater reclamation by utilizing a thin-film composite mixed matrix membrane with functionalized carbon nanotube blended polyethersulfone support layer. The study demonstrated that the membrane fouling was effectively prevented because of the repulsive interaction between the foulant and the membrane surface[90,91]. To enhance the performance of polyethersulfone (PES) membranes in water treatment, researchers have studied the use of carbon nanotube-blended PES membranes. The addition of multi-walled carbon nanotubes (MWCNTs) to the blend membranes can affect the morphology and permeation properties of the membranes. Modifying PES membranes with acid-functionalized carbon nanotubes (CNT) can increase the membrane flux by enlarging the pore size and surface area, improving rejection and thermal stability. While PES membranes have high thermal and chemical stability, they are prone to fouling because of their hydrophobicity. Consequently, they are not ideal for use in ultrafiltration and nanofiltration applications[92–94]. Vatanpour et al. studied the membrane filtration properties of PES/NH_2-MWCNT membranes regarding protein fouling and salt rejection. The highest rejection of Na_2SO_4, $MgSO_4$, and NaCl was 60%, 45%, and 20%, respectively, for 0.045 wt% PES/NH_2-MWCNT over 180 minutes. Salt solution pH affected MMM surface charge, roughness, and hydrophilicity, leading to a higher FRR during BSA filtration[95].

1.6 Surface Modification of Mixed Matrix Membranes

The surface modification of the prepared membrane imparts new properties such as improved separation efficiency, energy utilization, and chemical selectivity, which changes from those of unmodified membranes. This modification offers benefits like increased chemical resistance, pore size control, and removal of irregularities that enhance the flux or selectivity. The primary objective of surface modification is to improve permeability, antifouling properties, and hydrophilicity of the membrane surface. It also strengthens the chemical stability and imparts a surface charge to reject certain ions through the membrane. Surface modification can be achieved through various techniques like blending polymers and adding fillers before membrane preparation, however, plasma treatment, UV irradiation, coating from gas or wet phase, and grafting that involves covalent bond formation on the membrane surface.

1.6.1 Blending techniques

The modification of the membrane was achieved through the addition of fillers and polymeric materials to enhance the membrane properties. Nanoparticles, such as carbon nanotubes, graphene oxides, silica nanoparticles, and metal oxides, were used as fillers or additives. These fillers were added to the polymer matrix before membrane preparation. Another method is to use polymers as fillers, which is also known as blending two polymers to improve membrane characteristics. Polymers like Polyaniline[96], Polytetrafluoroethylene[97], β-CD Polyurethane[98], polyethylene glycol, polyvinylpyrrolidone (PVP), or polyethylene oxide-b-polypropylene oxide-b-polyethylene oxide were utilized for the modification of the membrane via blending. Blending polymers can result in a product with improved properties compared to the individual materials. However, the compatibility of the polymers is often the limiting factor. Common blends consist of hydrophobic materials with good mechanical and chemical stability paired with hydrophilic polymers[99,100]. In one experiment, blends of polysulphone and poly (ether sulphone) were synthesized using conventional solution casting and solvent evaporation techniques. The resulting membrane had a uniform morphology without any pores, while its permeability and selectivity values were between those of individual PSU and PES membranes. The addition of PES to PSU membranes improved their separation performance, leading to a 65% increase in selectivity in the PSU/PES blend membranes[101]. High-flux polyamide thin-film composite

(TFC) forward osmosis (FO) membranes with porous substrate layers made from PSU and PES blends with varying PSU/PES ratios were prepared, resulting in higher flux[102].

1.6.2 Bulk modification

A new approach for modifying membranes involves bulk modification, which alters the polymer structure rather than just the surface of the membrane. This can result in improved antifouling properties and increased hydrophilicity. However, using bulk modification methods may lead to a lower net effect since the entire membrane is modified, which could result in increased swelling in the membrane structure. Sulfonation, nitration, carboxylation etc. are commonly utilized methods for bulk modification of polymers. After sulfonation, commercial membranes are prepared and demonstrate improved properties such as membrane stability[103]. For example, the f-CNT/SPES mixed matrix membrane exhibits both better antifouling properties and increased tensile strength. The sulfonate functional group makes the membrane more hydrophilic and increases the negative charge on the surface, leading to better metal rejection. The process of sulfonating polyether sulphone involves the electrophilic aromatic substitution mechanism, in which the hydrogen atom in the benzene ring of polyether sulphone (PES) is replaced by a sulfonic acid group and is bonded to the ortho position in the aromatic ring with respect to the ether linkage in the polyether sulphone[104–107]. The presence of carboxylic groups can also increase the hydrophilicity of the membrane, much like sulfonic groups. This involves a similar substitution reaction, but with carboxylic groups as substituents. The addition of carboxylic groups enhances the hydrophilicity of the polymer, as demonstrated by water absorption measurements. This is due to the aryloxy groups, which are found in the main chain of many condensation polymers, aid in the electrophilic attack on the ortho position, while other groups like sulphone, hinder the activity of the adjacent rings[108,109]. The bisphenol A moiety in polysulphone appears to be more likely to undergo electrophilic substitution. A variety of functional groups have been introduced onto polysulphone through electrophilic substitutions such as sulfonation, bromination, halomethylation, nitration, and conversion of primary derivatives[110–112]. However, there are few reports on the chemical modification of polyether sulphone (PES), as its rings are strongly deactivated by electron-withdrawing sulfone groups, and this impeding effect is only slightly reduced by activating aryloxy groups[113].

1.6.3 Plasma treatment

Plasma treatment is widely used in modifying the surface of polymers. Polysulphone membranes can be modified through a plasma generated by ionizing a gas or water. The active components generated in the plasma can activate the upper molecular layers of the membrane surface to increase hydrophilicity without affecting the bulk of the polymer. Plasma treatment introduces functional groups on the membrane surface, and the characteristics of the surface can be controlled by varying the plasma treatment parameters[114–120].

1.6.4 UV irradiation

UV irradiation can occur either in the presence of water or methanol-soluble monomers, through the immersion technique. This approach involves immersing the membrane in a solution comprising vinyl monomers[121]. Radical sites are generated by UV irradiation in the solution, which react with the monomers to initiate polymerization. The presence of free radicals leads to a degree of polymerization of the monomers, ultimately resulting in their covalent attachment to the membrane. After irradiation, any remaining unreacted solution is removed by rinsing with deionized water[122–124].

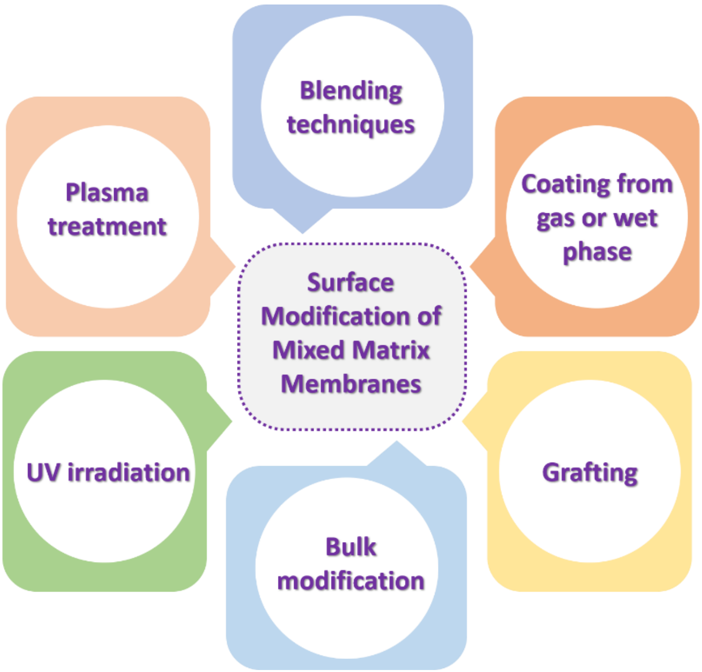


Figure 1.9. Surface Modification of membrane techniques

1.6.5 Coating from gas or wet phase

Membrane coating refers to a range of post-modification techniques that result in the formation of one or more layers on the membrane surface, without the creation of covalent bonds. Coating methods include gas coating, also known as vapour deposition, which involves multiple steps such as heating, evaporation, sputtering of vaporized materials, and deposition[125–127]. The surface of membranes can be coated with a polymer layer by using techniques like dip-coating or spin-coating, which is a popular approach for some commercial reverse osmosis membranes[128,129].

1.6.6 Grafting

Grafting is a surface modification technique used to chemically attach compounds on membrane surface. Unlike physical surface coatings, which may have limited long-term stability, grafted membranes have a stable chemical attachment of grafted entities through covalent bonding[130]. This allows for the decoration of the membrane surface with small molecular units or macromolecular species. There are two main approaches to grafting: "grafting-to" or "grafting-from." In the "grafting-to" approach, pre-fabricated species are bonded covalently to the membrane surface, such as polymer chains. In the "grafting-from" approach, polymer chains are grown directly from initiator sites on the membrane surface[131–134].

1.6.7 Chemical modification of membrane surface

The membrane surface properties impact the membrane performance, as the surface directly contacts the feed. Modifying the membrane surface through chemical methods can impart desirable surface properties while retaining the bulk polymer properties, such as mechanical and chemical resistance and membrane morphology. However, fouling or adsorption of undesirable species onto the membrane surface can lead to compromised membrane performance. Introducing new functionalities on the membrane surface can also improve fouling properties. As a result, much effort has focused on minimizing the unwanted accumulation of molecules on the membrane surface, which contains functional groups such as residual carboxylic acids and primary amines that can be exploited to graft specific functional groups. The chemical modification can create free radicals and ionic species, which act as the driving force for the attachment of the surface-modifying agents[135].

Among the aforementioned modification techniques, chemical modification is also employed, including controlled radical polymerization, redox-initiated grafting, and click chemistry. Reversible addition fragmentation chain transfer polymerization was used to graft porous AAO-silica onto a Poly-(Methacrylamidomethyl)-pyridine (PMAMP) membrane, resulting in a quaternized PMAMP-grafted composite membrane with high binding energies, good flexibility, and adsorption capacity[136]. Similarly, photoinduced electron transfer-reversible addition fragmentation chain transfer (PET-RAFT) was employed to introduce brush-like carboxybetaine methacrylate (CBMA) on a PVA hydrogel membrane, resulting in a biocompatible surface with good adhesion properties by increasing grafting on the membrane surface. This method has advantages such as low cost and low toxicity[137]. Two techniques - Atom Transfer Radical Polymerization (ATRP) and Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT) - have been employed to modify membranes, resulting in the creation of zwitterionic monomers on the surface of the membrane. The SI-eATRP method was utilized to graft polymer brushes onto a PES membrane, demonstrating that the modified membrane possessed better hydrophilic and anticoagulant properties compared to the unmodified PES membrane[138]. Previously, aqueous ATRP was carried out on a porous PVDF membrane at room temperature, leading to an improved hydrophilicity and a reduction in pore size distribution[139,140]. Additionally, zwitterionic polymers were bonded to a cellulose membrane via in situ ATRP, resulting in a modified membrane that displayed good resistance to protein and platelet adhesion[141]. By combining click chemistry with reversible addition-fragmentation chain transfer radical polymerization, a novel three-step technique was developed to graft polyacrylamide onto a polypropylene macroporous membrane. This modification gives a hydrophilic membrane surface and improved protein rejection because of the presence of functional groups on the surface[142]. Similarly, in a two-step process, zwitterionic sulfobetaine groups were grafted onto a polysulfone (PSU) membrane using 2-azidoethyl methacrylate and N, N-diethyl-N-propargyl-N-(3-sulfopropyl) ammonium (DEPAS) via surface-initiated atom transfer radical polymerization (ATRP) and click reactions. The resulting polysulfone membrane became more resistant to bovine serum albumin and showed better adhesion properties[143].

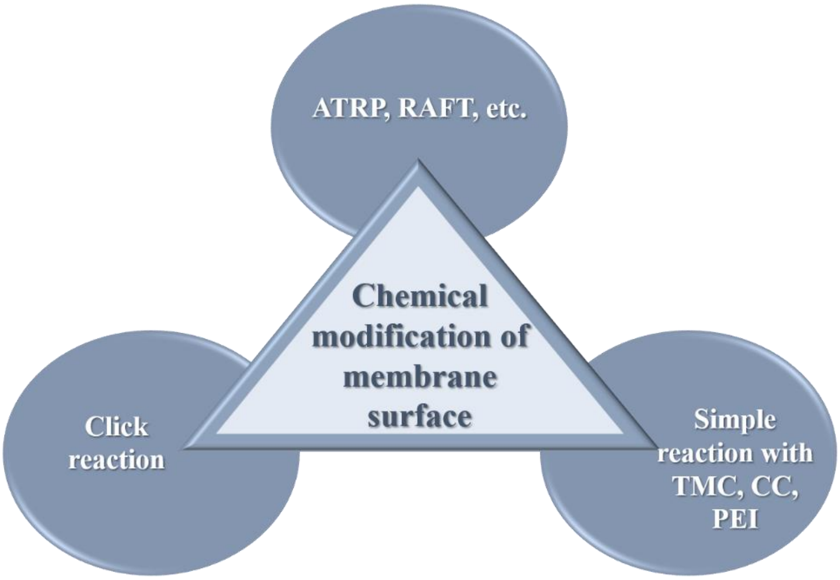


Figure 1.10. Chemical modification techniques

1.6.8 Surface modification via click reaction

The Cu(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition, commonly referred to as the 'click reaction,' takes place in a single pot and is not affected by water. It generates minimal and harmless byproducts and is characterized by a high thermodynamic driving force that drives it quickly and irreversibly to a high yield of a single reaction product with high selectivity. This reaction serves as the most powerful and versatile click reaction. The Cu-catalyzed azide-alkyne cycloaddition reaction results in the formation of 1,2,3-triazoles through a copper catalyzed reaction. This reaction is exothermic and occurs efficiently in both protic and aprotic solvents, including water. However, the reaction is highly exothermic, and its high activation barrier makes it slow[144]. A click reaction applied to pristine polysulfone membranes results in a more hydrophilic surface compared to unmodified polysulfone membranes[145]. Modifying the surface of a polyethersulfone/azide-CNT mixed-matrix membrane through a click reaction provides a hydrophilic surface with improved antifouling properties. This membrane showed better heavy-metal rejection and enhanced antifouling properties[146]. The presence of triazole rings on the polysulfone/azide-CNT mixed-matrix membrane surface, which results from a click reaction, increases hydrophilicity and heavy metal rejection. The introduction of a triazole moiety on the membrane surface also enhances its antifouling properties[147].

1.6.9 Surface modification using trimesoyl chloride (TMC) and cyanuric chloride (CC)

The improvement of membrane separation and antifouling properties involves the use of trimesoyl chloride (TMC) and cyanuric chloride for surface modification. TMC is commonly used as a monomer to create thin film composite (TFC) membranes. On the other hand, cyanuric chloride results in the formation of a polymer with reduced hydrolysis-prone amide bonds, leading to improved membrane stability[148]. Interfacial polymerization is a widely used technique for membrane modification. For instance, TMC in combination with 1,3,5-(tris-piperazine)-triazine was used to produce poly(s-triazine-amine) NF membranes[149]. Another approach involved modifying the properties and performance of polyethyleneimine nanofiltration membranes by using a polyethylenimine-dextran conjugate[150]. Modified membranes underwent systematic characterization to evaluate changes in properties and separation performance, with experimental results indicating overall improved membrane performance. Cyanuric chloride and trimesoyl chloride are advantageous in membrane modification. Cyanuric chloride is stable and pH resistant, making it a preferred option. Trimesoyl chloride is widely used in thin-film composite (TFC) membrane fabrication and offers advantages such as widespread application, utilization in interfacial polymerization techniques, and enhancement of membrane properties and performance. However, limitations include concerns about toxicity, high costs, and handling and disposal challenges. The selection of the appropriate monomer depends on specific application requirements and desired membrane properties. Despite the limitations in reactivity and the limited amount of research conducted compared to other monomers, the utilization of cyanuric chloride for membrane modification remains a viable option. One way to overcome its limitations in reactivity is by combining it with amines. It is worth noting that the application of cyanuric chloride in membrane modification is a relatively recent area of research, and there is still much to be explored regarding its performance and properties in comparison to other monomers.

The primary objective of membrane surface modification is to increase its functionality, which in turn improves its ability to remove heavy metals efficiently and provides other desirable properties, such as antifouling. Modifying the membrane surface incorporates functional groups, such as 1,3,5-triazines and 1,3,5-benzenetricarbonyls, that have an affinity for heavy metals. These functional groups selectively interact with heavy-metal ions, promoting their adsorption and retention on the membrane surface. This allows for effective separation and rejection of heavy metals from the feed solution passing through the membrane. The incorporation of these functionalities enhances the separation characteristics of the membrane, leading to improved heavy metal rejection efficiency. Additionally, surface modification can improve the antifouling properties of the membrane.

1.6.10 Surface modification with Polyethylenimine (PEI)

Positively charged membranes have various applications, including cation separation, removal of multivalent cations, and removal of metal ions. These membranes can be synthesized by functionalizing ready-made membranes with polyelectrolytes, such as hyperbranched polyethyleneimine (PEI)[151–153]. Hyperbranched polyethylenimine (HPEI) has been added to PES-based membranes to enhance their ultrafiltration, antibacterial, and antifouling properties[154]. Aromatic polyamide RO membranes have been modified with PEI of different molecular weights to alter the surface charge and create a positively charged membrane with high anti-fouling properties[155]. A positively charged NF membrane has been prepared by evaporation deposition and the reaction of PEI on the surface of the C-PES/PES blend UF membrane[156]. Surface grafting with PEI involves attaching PEI to the surface of a substrate or material, which can enhance the interfacial properties of composites, create protein-resistant surfaces, and modify the surface properties of the substrate[157–159]. Membrane fouling can negatively impact water treatment systems by reducing productivity, increasing energy costs, altering membrane selectivity, reducing water quality, and potentially causing irreversible damage. However, various methods can be employed to mitigate the effects of fouling. One approach is to modify the membrane surface with PEI and zwitterionic polymers, which have been shown to enhance the antifouling properties. Techniques such as surface modification with PEI and zwitterionic polymers, grafting, layer-by-layer assembly, and rapid modification have been used to achieve these modifications. A study conducted by researchers synthesized a zwitterionic polymer called PEI-CA and grafted it onto the surface of polyamide reverse osmosis (RO) membranes, resulting in the membranes exhibiting antifouling properties[160]. Another study aimed to create antifouling thin-film composite nanofiltration (TFC-NF) membranes by first grafting PEI to the membrane surface and then undergoing zwitterionic modification, which gives improved antifouling towards charged foulants like negatively charged Bovine serum albumin and positively charged Lysozyme[161]. The modification of nanofiltration membranes with zwitterions on their surface has been demonstrated to enhance their antifouling properties. This involves creating a "buffer layer" on the membrane surface. This modification can be achieved through various methods such as layer-by-layer assembly. An alternative approach was adopted in a study in which the surface properties of ultrafiltration membranes were modified using a solvent-free method called PECVD. This rapid modification aimed to improve the antifouling resistance of the membranes[162,163]. The surface charge affects the efficiency of heavy metal removal through mechanisms such as adsorption, complexation-ultrafiltration, electrostatic repulsion, and pore sieving. Modifying the membrane surface to tune a suitable charge can enhance heavy metal ion removal from water. Modifying the surface charge of membranes is an effective way to enhance heavy metal removal efficiency[164–166]. Materials such as PEI, silica-poly (ionic liquid) nanoparticles, layered clay materials, and adsorbed coatings can be used to modify the surface charge of membranes for heavy-metal removal[167–169]. Positively charged membranes, such as those modified with PEI, can effectively remove heavy metal ions from waste-water. A PEI/TMC membrane modified with an ionic liquid exhibited enhanced permeability and antibacterial properties for the rejection of heavy metal ions. The positively charged membrane effectively reject heavy metal ions from contaminated water[170]. A review of recent advances in membranes used for nanofiltration to remove heavy metals from wastewater highlights that the surface modification of membranes can improve their heavy-metal removal performance. For example, a modified polyetherimide (PEI) nanofiltration membrane with a chemical surface-coating approach is effective for rejecting heavy metals from aqueous solutions. A modified polyvinylidene fluoride membrane coated with epoxied SiO2 nanoparticles and PEI adsorbed heavy metal ions in water and rejected them via filtration. The modified membrane had a highly positively charged surface, resulting in enhanced the removal of heavy-metal ions[171].

1.7 Waste-water treatment

Water is vital for supporting life on Earth and plays a crucial role in ecological, industrial, agricultural, and domestic activities. Access to clean and safe water is essential for human health, food production, sanitation, and economic development. However, increasing demand and industrialization pose a risk to the quality of water resources, as they are at risk of contamination from various pollutants, including heavy metals. Heavy metals like lead, mercury, cadmium, chromium, and arsenic are highly toxic and can accumulate in water bodies and disrupt aquatic ecosystems. Human activities, particularly industrial processes, mining, and improper waste disposal, are the primary contributors to heavy metal contamination. Exposure to heavy metals can result in severe health issues, including neurological disorders, kidney damage, and cancer. Acknowledging the urgency of addressing heavy metal pollution, researchers and environmentalists have developed advanced treatment methods to ensure the rejection of heavy metals from wastewater before it is released into natural water bodies.

Heavy metals like mercury, cadmium, chromium, copper, lead, and arsenic can cause severe damage even at low concentrations. They are naturally occurring elements with high atomic weight and density that exceed water's by at least five times. Some heavy metals have biological functions in living organisms, while others are non-essential and have unknown biological functions. These metals can enter the environment through natural processes or human activities like mining, industrial production, and untreated sewage disposal. To prevent harmful accumulation of heavy metals in the human body, it is crucial to actively reject them. Minimizing heavy metal pollution requires reducing usage, proper waste disposal, recycling, soil and water treatment, and effective legislation and guidelines. Several techniques like chemical precipitation, adsorption, ion exchange, electrochemical deposition, and membrane filtration are used to reject heavy metals from wastewater and are efficient in eliminating them. These methods can be used in combination to enhance outcomes.

Membrane filtration is an extremely efficient technique for removing heavy metals from wastewater. Commonly used membrane filtration methods include nanofiltration, reverse osmosis, ultrafiltration, and forward osmosis. These methods effectively remove divalent metal ions, such as lead, copper, and cadmium. The extent to which heavy metals are rejected depends on factors like the pH and ionic strength of the wastewater, as well as the specific type of membrane employed. Several parameters affect the efficacy of heavy metal rejection via membrane filtration, including the feed pH, ionic strength, heavy metal concentration, membrane type, operating time, and surface charge. The optimal parameters must be determined for each heavy metal and membrane combination to attain the highest rejection efficiency. The surface charge of the membrane can be modified by introducing functional groups on the membrane surface or by adjusting the pH of the wastewater, thereby impacting the rejection performance. Temperature also plays a role in heavy metal rejection via membrane filtration, with the effectiveness varying depending on the specific metal and membrane type. Some heavy metals may be more effectively removed at higher temperatures, while others exhibit improved removal at lower temperatures[172–174].